DOI: 10.1002/adsc.201100684

Changing the Palladium Coordination to Phosphinoimidazolines with a Remote Triazole Substituent

Verónica de la Fuente,[a] Rocío Marcos,[b] Xacobe C. Cambeiro,[b] Sergio Castillón,[c,*] Carmen Claver,[a,*] and Miquel A. Pericàs[b,d,*]

[a] Departament de Química Física i Química Inorgànica, Universitat Rovira i Virgili; C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain
Fax: (+34)-977-559-563; phone: (+34)-977-559-574; e-mail: carmen.claver@urv.cat
[b] Institute of Chemical Research of Catalonia (ICIQ); Av. Països Catalans 16; 43007 Tarragona, Spain
Fax: (+34)-977-920-222; phone: (+34)-977-920-200; e-mail: mapericas@iciq.es
[c] Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili; C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain
E-mail: sergio.castillon@urv.cat
[d] Departament de Química Orgànica, Universitat de Barcelona; 08028 Barcelona, Spain

Received: July 17, 2011; Revised: August 29, 2011; Published online: December 6, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adcs.201100684.

Abstract: Phosphinoimidazoline (PHIM) ligands bearing a triazolylmethyl substituent at the sp^3 nitrogen atom in the imidazoline ring lead to highly improved enantioselectivity (up to 99% *ee*) in allylic substitution reactions with respect to analogous ligands with substituents lacking the triazole unit. NMR and theoretical studies support a shift in the coordination mode of the PHIM ligand to palladium, triggered by a very favourable interaction with the triazole unit.

Keywords: allylic substitution; asymmetric catalysis; palladium; phosphinoimidazoline ligands; triazole ligands

Phosphinooxazolines (PHOX)[1] are versatile C_1-symmetric chiral ligands (Figure 1, *left*) with ample applications in a variety of metal-catalyzed reactions. The analogous phosphinoimidazoline (PHIM) ligands (Figure 1, *right*) could represent an even more convenient alternative: the topology of the imidazoline ligand allows the use of readily available C_2-symmetric diamine fragments, while the second nitrogen atom represents an additional source of molecular diversity (R^2), allowing the programmed modification of the electronic properties of the coordinating nitrogen atom. The additional nitrogen atom could also serve for the heterogenization of the phosphinoimidazoline ligand onto insoluble organic resins, a field which still remains completely unexplored.

PHIM ligands have shown to be very efficient in the Ir-catalyzed enantioselective hydrogenation of prochiral olefins[2] and imines,[3] as well as in the Pd-catalyzed asymmetric Heck reaction.[4] However, they have never been used in Pd-catalyzed asymmetric allylic substitution reactions, a domain where PHOX ligands are one of the most important players.[1d,5] We wish to report in the present paper the structural optimization of modular PHIM ligands using the Pd-catalyzed asymmetric allylic substitution reaction as a benchmark. A first generation of PHIM ligands results from the optimization of the substituents at C-4 and C-5 on the imidazoline moiety (R^1), the substituent at the non-coordinating nitrogen atom of the imidazoline ring (R^2), and the substituents of the phos-

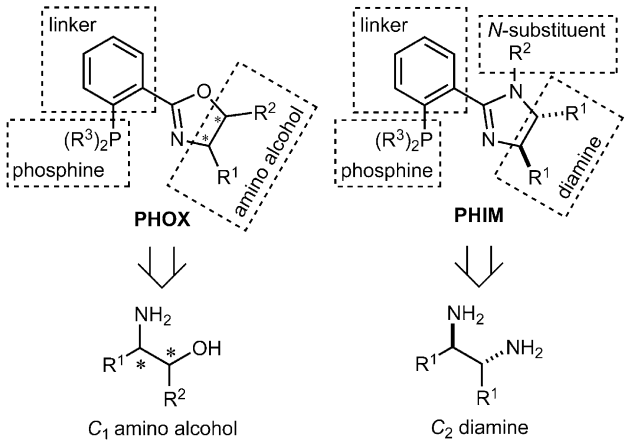
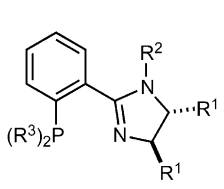


Figure 1. Modular phosphinooxazoline (PHOX) and phosphinoimidazoline (PHIM) ligands.



1	R^1,R^1 = Ph, Ph	R^2 = H	R^3 = Ph
2	R^1,R^1 = -$(CH_2)_4$-	R^2 = H	R^3 = Ph
3	R^1,R^1 = Ph, Ph	R^2 = Bn	R^3 = Ph
4	R^1,R^1 = -$(CH_2)_4$-	R^2 = Bn	R^3 = Ph
5	R^1,R^1 = Ph, Ph	R^2 = *n*-Pr	R^3 = Ph
6	R^1,R^1 = Ph, Ph	R^2 = Ts	R^3 = Ph
7	R^1,R^1 = Ph, Ph	R^2 = H	R^3 = Cy

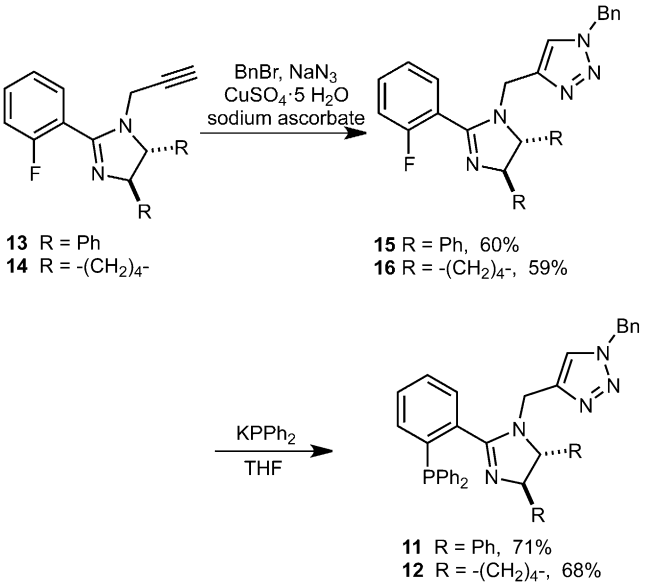
Figure 2. First generation PHIM ligands **1**–**7**.

phine moiety (R^3). A second generation of PHIM ligands, resulting from the introduction of triazolylmethyl moieties as nitrogen substituents (R^2), has unexpectedly led to catalytic systems with highly improved enantioselectivities for a variety of substrates and nucleophiles. A combined theoretical and NMR study provides a satisfactory explanation for this behaviour.

A small modular library of phosphinoimidazoline ligands **1**–**7**, including variations of the employed C_2-symmetrical 1,2-diamine, the diorganylphosphino moiety, and the substituent at the sp^3-type nitrogen atom in the imidazoline was initially prepared by standard methodology[3,6] (Figure 2, see Supporting Information for details).

With these ligands in hand, the alkylation of (*E*)-1,3-diphenylallyl acetate (**8**) with dimethyl malonate and the amination of the same substrate with benzylamine in the presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ were taken as model reactions (Table 1). For the alkylation reaction, optimal reaction conditions involved working in dichloromethane, with microwave irradiation at 65 °C, in the presence of KOAc and BSA (Table 1, entries 1–7, Conditions A). Under these conditions, all the ligands tested resulted in good conversion in a reasonable reaction time. In terms of enantioselectivity, *N*-benzylated ligands **3** and **4** (entries 3 and 4), gave the best results (85 and 87% *ee*, respectively), with little influence of the 1,2-diphenylethylene or cyclohexane-1,2-diyldiamine backbones being used. On the other hand, comparison of ligands **1** and **7** (entries 1 and 7) shows that the diphenylphosphino moiety provides better results than the dicyclohexylphosphino one. The corresponding amination reaction with benzylamine was next studied with the most synthetically interesting *N*-substituted ligands **3** and **4** (Table 1, entries 8 and 9, Conditions B). While satisfactory conversions were registered under thermal conditions, enantioselectivity was only *ca.* 80%.

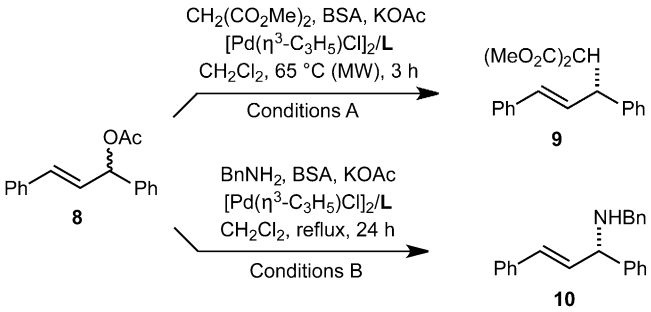
Having in mind the ultimate goal of supporting the PHIM ligands onto polymer supports for easy recovery and recycling,[7,8] we decided to study the catalytic behaviour of PHIM derivatives bearing triazolylmethyl substituents on the imidazoline moiety. Thus, ligands **11** and **12** were prepared through CuAAC reactions[9] from *N*-propargylic derivatives **13** and **14** (Scheme 1). The triazole moieties were installed by



13 R = Ph
14 R = -$(CH_2)_4$-
15 R = Ph, 60%
16 R = -$(CH_2)_4$-, 59%
11 R = Ph, 71%
12 R = -$(CH_2)_4$-, 68%

Scheme 1. Synthesis of second-generation PHIM ligands **11** and **12**.

Table 1. Alkylation and amination of 1,3-diphenylallyl acetate (**8**) with Pd/PHIM catalysts.

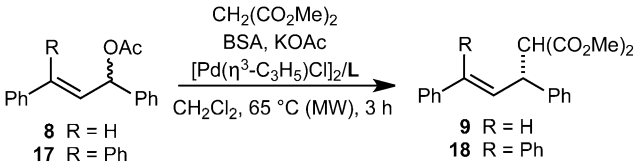


Entry	Ligand	Conditions[a]	Conversion [%][b]	*ee* [%][c]
1	**1**	A	100	83
2	**2**	A	91	53
3	**3**	A	71	85
4	**4**	A	88	87
5	**5**	A	99	81
6	**6**	A	100	73
7	**7**	A	74	78
8	**3**	B	95	79
9	**4**	B	100	82

[a] All reactions run with 0.02 mmol $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 0.044 mmol ligand, 1 mmol substrate, 3 mmol dimethyl malonate (Conditions A) or 3 mmol benzylamine (Conditions B), 3 mmol BSA and 0.04 mmol KOAc in 2 mL CH_2Cl_2.
[b] By NMR.
[c] By HPLC on a chiral stationary phase.

reaction with benzyl bromide in the presence of sodium azide, L-ascorbic acid and catalytic amounts of $CuSO_4$, and the phosphino units were introduced in

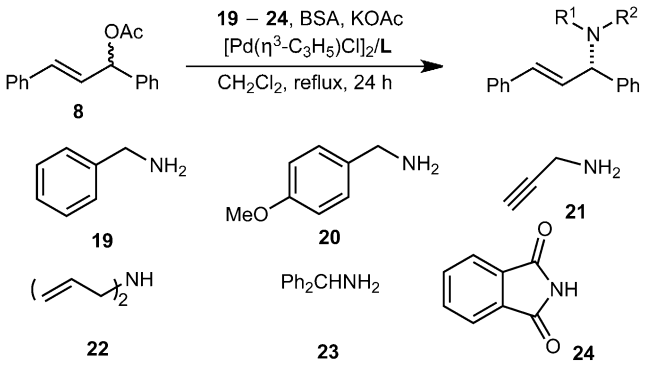
Table 2. Pd-catalyzed allylic alkylation with second generation PHIM ligands **11** and **12**.[a]



Entry	Substrate	Ligand	Conversion [%][b]	*ee* [%][c]
1	**8**	**11**	94	96
2	**8**	**12**	85	86
3	**17**	**11**	63	99
4	**17**	**12**	32	75

[a] All reactions run with 0.02 mmol $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 0.044 mmol ligand, 1 mmol substrate, 3 mmol dimethyl malonate, 3 mmol BSA and 0.04 mmol KOAc in 2 mL CH_2Cl_2.
[b] By NMR.
[c] By HPLC on a chiral stationary phase.

Table 3. Pd-catalyzed allylic amination with second generation PHIM ligands **11** and **12**.[a]



Entry	Ligand	Nucleophile	Conversion [%][b]	*ee* [%][c]
1	**11**	**19**	99	98
2	**11**	**20**	99	96
3	**11**	**21**	99	96
4	**11**	**22**	99	99
5	**11**	**23**	99	97
6[d]	**11**	**24**	47	99
7	**12**	**19**	99	84
8	**12**	**22**	49	67
9[d]	**12**	**24**	0	–

[a] All reactions run with 0.02 mmol $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 0.044 mmol ligand, 1 mmol substrate, 3 mmol nucleophile, and 3 mmol BSA in 2 mL CH_2Cl_2.
[b] By NMR.
[c] By HPLC on a chiral stationary phase.
[d] 48 h.

the last step of the sequence to prevent oxidative deterioration of the PHIM ligands.

The performance of ligands **11** and **12** was first examined in the alkylation of substrates **8** and **17** with dimethyl malonate under the previously optimized reaction conditions. The results (Table 2) showed the 1,2-diphenylethylenediamine-derived ligand **11** to be clearly superior to the 1,2-cyclohexanediamine-derived one **12**, both in terms of catalytic activity and enantioselectivity. In addition, and quite notably, these *N*-triazolylmethyl PHIM ligands turned out to induce notably higher enantioselectivities than their *N*-alkyl or unsubstituted counterparts (see Table 1, *above*).

Ligands **11** and **12** were also tested in the palladium-catalyzed allylic amination of **8** using amines **19**–**24** (Table 3). The results confirmed that the structure of **11** incorporates the optimal chiral fragment for high enantioselectivity in the amination reaction. Very remarkably, when this ligand was used for the amination with synthetic equivalents of ammonia (**19**, **22**, **23**), complete conversion with virtually complete enantioselectivity was recorded. In fact, the enantioselectivities achieved with ligand **11** are among the highest reported for this type of reaction.[10]

The very positive effect on enantioselectivity of a triazolylmethyl substituent at the sp^3 nitrogen atom of the imidazoline ring in PHIM ligands is hardly understandable by analysis of the generally accepted transition states for the Pd-catalyzed substitution reactions, since the aromatic part of the substituent on the imi-

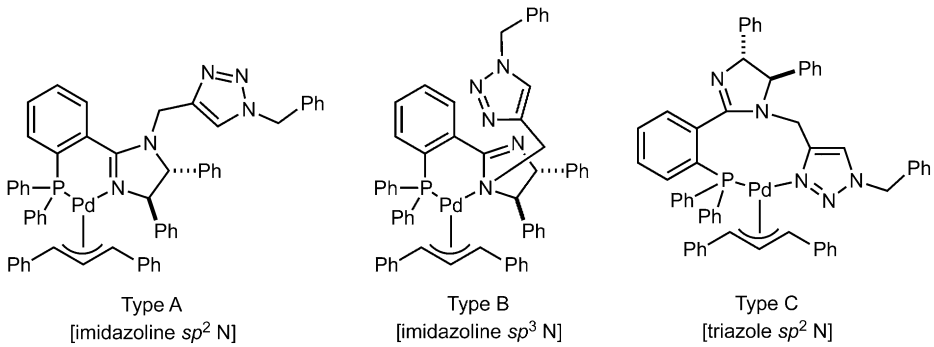


Figure 3. Alternative coordination modes in [Pd (η^3-C_3H_5) (PHIM)]$^+$ cationic complexes. The nature of the coordinating N atom is shown in brackets.

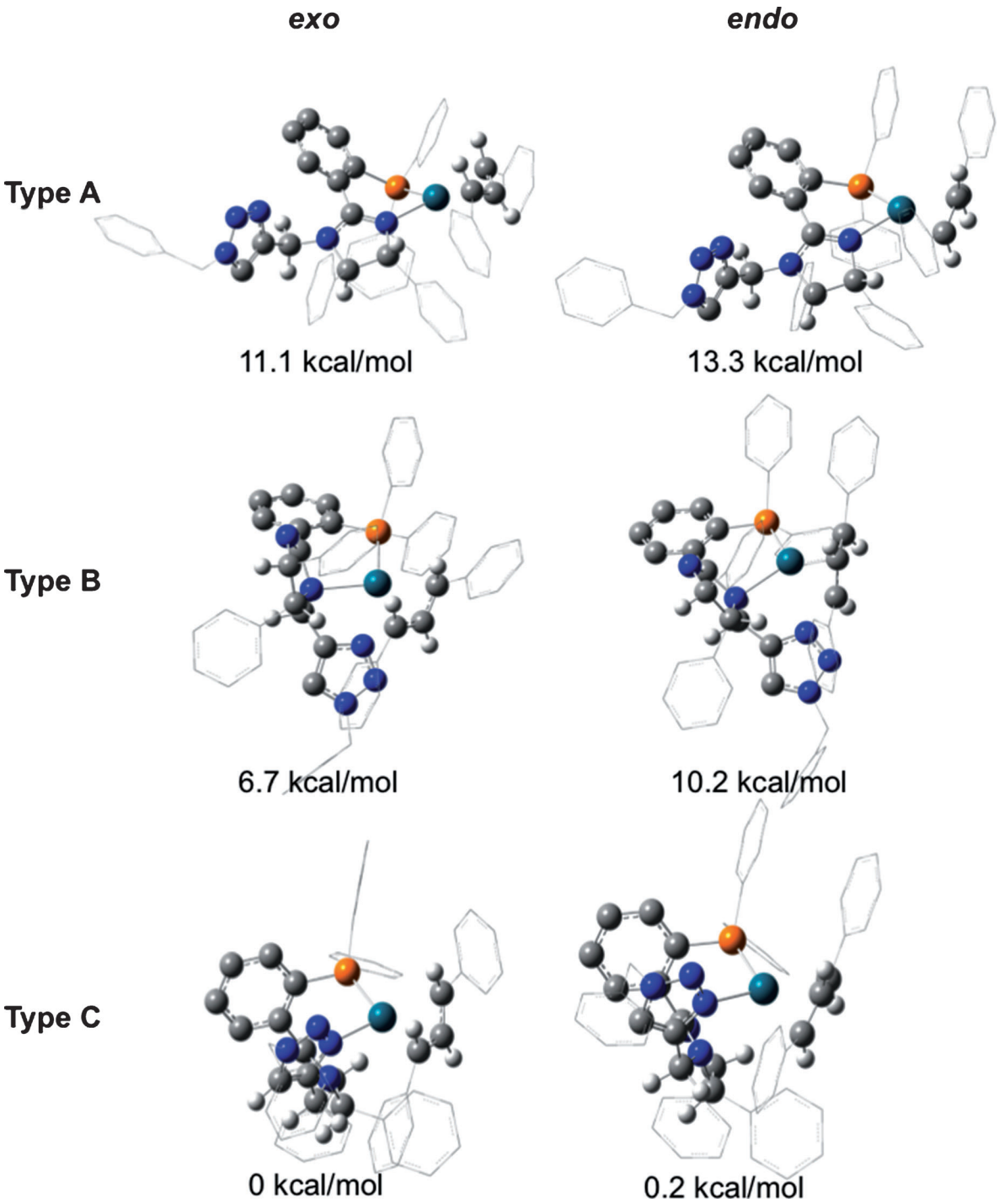


Figure 4. DFT-optimized structures and energies of the [Pd(η^3-diphenylallyl)(**11**)]$^+$ cationic complex. Non-relevant hydrogen atoms have been omitted for clarity. Exoskeletal substituents are represented as a wireframe; green: Pd; orange: P; blue: N; grey: C; white: H.

dazoline N-1 position is both electronically isolated and spatially remote from the molecular region where the bond-making process takes place (Figure 3, type **A**). This led us to speculate with the possibility of the triazolylmethyl substituent triggering a change in the coordination mode of the phosphinoimidazoline with palladium, from the usual N-3 nitrogen atom of the imidazoline to the N-1 one (type **B**) or even to the triazole group (type **C**).[11,12]

To test this hypothesis, we decided to study by theoretical means (DFT) the η^3-(1,3-diphenylallyl)palladium intermediates arising from the three proposed

coordination modes of the PHIM ligand to palladium. For each coordination mode, *exo* and *endo* isomers of the *syn-syn* type were considered. The calculations were performed with the Minnesota 06 (M06) functional,[13] as implemented in Gaussian 09.[14] The triple-ζ Stuttgart–Dresden (SDD) basis set and effective core potentials[15] were used for palladium and the split-valence double-ζ 6-31G basis set with additional *d* polarization functions[16] for all the other atoms. After an exhaustive conformational analysis, absolute energy minima for the *endo* and *exo* isomers of the three coordination modes were located and characterized. To simulate the employed experimental conditions, single point energy calculations were performed on the optimized structures with the scrf solvent model[17] for dichloromethane. The results, summarized in Figure 4, surprisingly revealed an extremely strong stabilization of the type **C** structures with respect to the *normal* type **A** ones (>11 kcal mol^{-1}) as well as with respect to the type **B** ones (>6 kcal mol^{-1}). This result clearly indicates the triazole to be a good ligand for palladium, thus allowing it to be significantly competitive even in this situation where the imidazoline coordination leads to a very stable six-membered chelate ring.

To check this conclusion against experimental data, we decided to study in detail the cationic Pd(II) complex [Pd(η^3-diphenylallyl)(**11**)]PF_6, which could be easily obtained upon treatment of **11** with the dimeric precursor [Pd(η^3-diphenylallyl)Cl]$_2$ and NH_4PF_6. Unfortunately, no crystals suitable for X-ray analysis could be obtained; however, a comprehensive NMR study (see Supporting Information) provided strong support to the conclusions of the theoretical study.

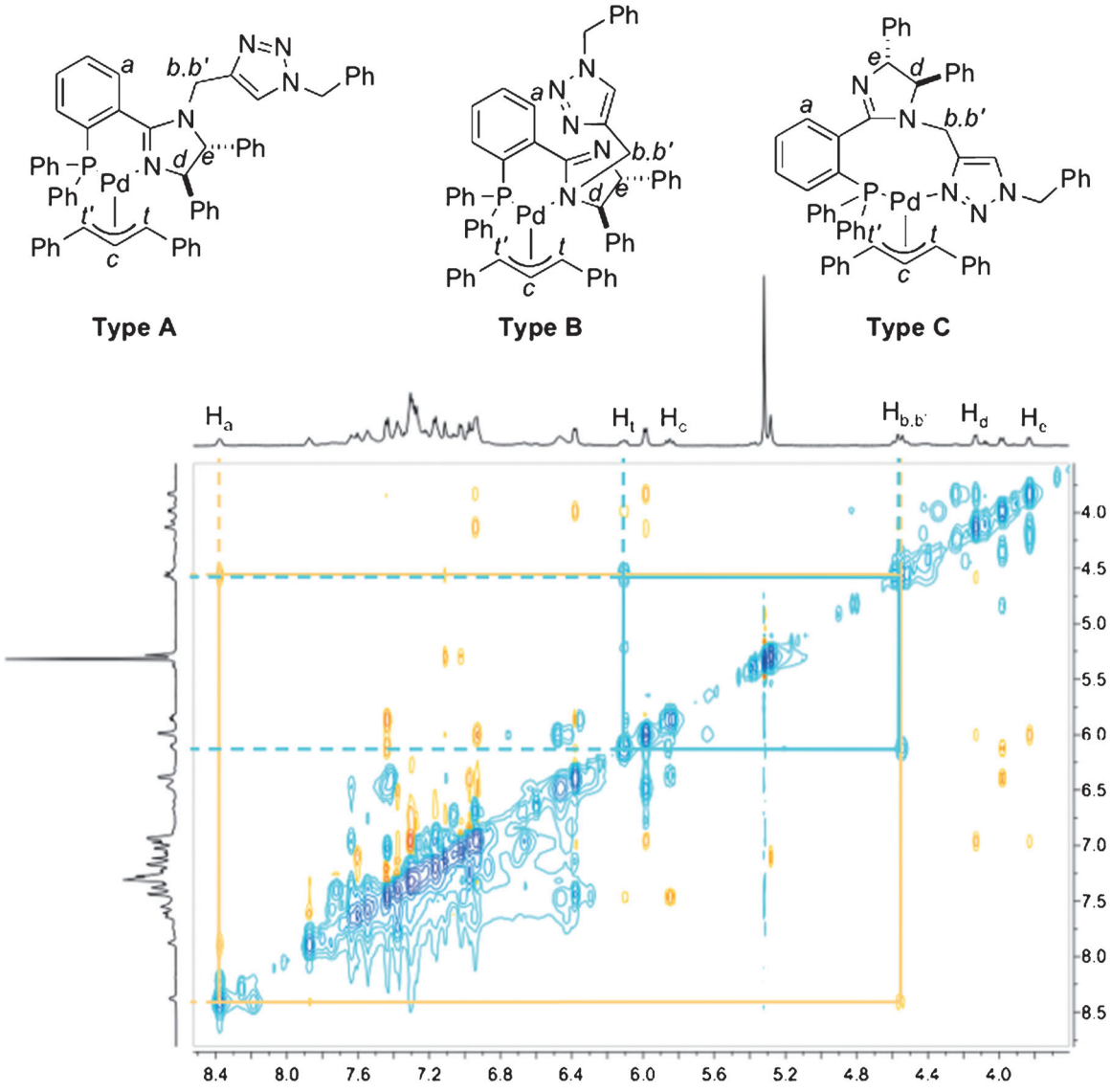


Figure 5. NOESY spectrum of the [Pd(η^3-diphenylallyl)(**11**)]PF_6 complex in CD_2Cl_2. Peaks in yellow correspond to positive NOEs and peaks in blue to negative ones, likely indicating an exchange process to be taking place (*endo-exo* interchange).

Particularly remarkable are the results of NOESY experiments (Figure 5), which showed significant differences with complexes of PHIM ligands lacking the triazolylmethyl moiety. Namely, (*i*) in contrast with what observed for alkyl-substituted PHIM ligands (**5**, see Supporting Information), an NOE interaction between one of the methylene hydrogens ($H_{b'}$) in the triazolylmethyl substituent and the allyl terminal hydrogen in a position *trans* to phosphorus (H_t) was observed for [Pd(η^3-diphenylallyl)(**11**)]PF_6, and (*ii*) also in contrast with what observed for alkyl-substituted PHIM ligands, no NOE between the imidazoline C-4 or C-5 hydrogens (H_d and H_e) and the allyl hydrogens (H_t and H_c) was observed for [Pd(η^3-diphenylallyl)(**11**)]PF_6.

If we consider type **A** structures resulting from the theoretical study, the very long distances between $H_{b'}$ and H_t (7.23 Å in **A**-*exo* and 7.59 Å in **A**-*endo*) would prevent the observation of NOE interactions between these protons. In addition, the rather short distances between H_d and H_t (2.97 Å in **A**-*exo* and 3.77 Å in **A**-*endo*) should result in the observation of NOE interactions between these protons. According to these observations, type **A** structures involving the normal coordination of the imidazoline to palladium must be discarded.

In type **B** structures, significant NOE interactions should be expected between H_e and the close H_c and H_t protons on the allyl moiety (the calculated distances between H_e and H_t are 3.51 Å in **B**-*exo* and 2.88 Å in **B**-*endo*). However, these interactions are not observed experimentally with [Pd(η^3-diphenylallyl)(**11**)]PF_6, and this is a solid argument against type **B** structures.

Finally, a thorough analysis of the geometrical characteristics of type **C** minima and of the results obtained in the NOESY experiments with [Pd(η^3-diphenylallyl)(**11**)]PF_6 revealed a perfect correlation between both sets of data (Table 4). Since type **C** structures are the most stable ones according to theoretical calculations, the results of the combined NMR and DFT study provide a rather solid support for the proposed change of the coordination mode of **11** to palladium, with the triazole unit instead of the imidazoline moiety coordinatively bonded to the metal.

In conclusion, PHIM ligands bearing a 4-(1,2,3-triazolyl)methyl substituent at the N(sp^3) atom in the imidazoline ring, have been shown to be much more efficient chiral controllers (up to 99% *ee*) than the corresponding analogues lacking the triazole group in Pd-catalyzed allylic substitutions (*ca.* 80% *ee*). A combined NMR and DFT study has shown that these P,N ligands most likely coordinate to palladium through the triazole N-3 nitrogen atom as the N component, giving rise to a highly asymmetric, unprecedented structure with increased bite angle, and with one of the faces of the chelate plane very efficiently shielded by the imidazoline moiety. This new coordination behaviour offers potential for the design of P,N ligands with increased catalytic efficiency and enantioselectivity in different reaction types. Work along these lines is now in progress in our laboratories.

Table 4. NOE-relevant H-H distances in the calculated minimal energy conformers of the [Pd(η^3-1,3-diphenylallyl)(**11**)]$^+$ cationic complex and its comparison with the observed NOE's in the NMR study of the same complex.[a]

H	H	NOE observed?	Distance [Å]					
			A_{exo}	A_{endo}	B_{exo}	B_{endo}	C_{exo}	C_{endo}
H_a	H_b	YES	2.36	2.43	3.67	3.53	3.15	3.17
H_a	$H_{b'}$	YES	3.77	3.82	4.05	3.59	4.66	4.68
$H_{b'}$	H_t	YES	***7.23***	***7.59***	4.55	***5.59***	3.61	4.89
H_t	H_d	NO	***2.97***	***3.77***	6.28	***4.81***	5.03	7.21
H_t	H_e	NO	5.52	6.38	***3.51***	***2.88***	5.24	7.05
H_c	H_d	NO	***4.78***	***4.83***	5.70	6.96	7.07	5.36
H_c	H_e	NO	7.45	6.73	***3.79***	***4.37***	7.74	5.80

[a] Highlighted in boldface italics are the distances considered not to be consistent with the experimental data. For this simplification we have assumed a cut between observable or not observable NOE at 5.00 Å, which is a somewhat extreme, although valid distance.[18]

Experimental Section

General Procedure for the Palladium-Catalyzed Allylic Substitution of 8 and 17 with Different Nucleophiles using the Pd/11 Catalytic System

To a Schlenk tube under argon, [Pd(η^3-C_3H_5)Cl]$_2$ (1.84 mg, 5 μmol, 2%) and ligand **11** (0.011 mmol) in CH_2Cl_2 (2 mL) were introduced. The resulting solution was stirred for 20 min. Then, the substrate (250 μmol), the nucleophile (750 μmol), BSA (185 μL, 750 μmol) and 5 μmol KOAc were successively added. The mixture was stirred under reflux conditions until reaction completion. The reaction mixture was then diluted with diethyl ether, filtered over Celite, and washed with water (3×5 mL). The organic phase was dried over anhydrous $MgSO_4$. The residue was purified through a short SiO_2 pad eluting with (hexane/EtOAc from 100:0 to 80:20). Conversion was determined by ^{1}H NMR of the crude product after solvent removal under vacuum.

Acknowledgements

We thank MICINN (Grants No. CTQ2007-62288/BQU and CTQ2008-00947/BQU), AGAUR (Grant No. 2009SGR623), Consolider Ingenio 2010 (Grant No. CSD2006-0003), ICIQ Foundation and GC (Distinction for Research Promotion 2003 CC) for financial support. V. dlF and R. M. are grateful to GC and MICINN, for predoctoral fellowships. We are also grateful to R. Guerrero and M. A. Rodríguez (SRCT, URV) and Dr. C. Godard for assistance and advice in NMR studies

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