DOI: 10.1002/ejic.201100113

Synthesis, Coordination Properties and Application of New *N*,*N*-Ligands Based on Bornyl and Binaphthylazepine Chiral Backbones in Palladium-Catalyzed Allylic Substitution Reactions

Giovanni Bottari*[a][‡] Angelo Meduri,[a][‡‡] Dario Drommi,[a] Giovanna Brancatelli,[a] and Felice Faraone[a]

Keywords: Palladium / N ligands / Allylic compounds / Asymmetric catalysis / Enantioselectivity

The synthesis of new imine-amine and diamine ligands, based on both the atropisomeric (S_a)- or (R_a)-1,1′-binaphthyl and (*R*)-bornyl backbones, and incorporating an ethylenediamino spacer, are reported. In addition, analogue ligands in which one chiral arm is replaced by the achiral NMe_2 group were synthesized. These *N*,*N*-ligands when coordinated to a palladium metal centre form highly enantioselective catalysts for the asymmetric allylic alkylation of *rac*-2-acetoxy-1,3-diphenylpropene by dimethyl malonate. In one case, the synergic effect of the chirality elements in the palladium catalyst afforded the (*S*) substitution product with an enantiomeric excess (*ee*) of >99%. Based on NMR studies of the active species in solution, a reliable explanation for the origin of the enantioselectivity of these palladium catalysts is also provided.

Introduction

Stereoselective formation of C–C bonds is a major challenge in synthetic chemistry and transition metal complexes may serve as a powerful tool to control the selectivity of such processes.[1] In this field, allylic substitution reactions have played a dominant role over the years thanks to their mild experimental conditions and low metal-catalyst loading requirements; moreover, depending on the nature of the chiral inducer, the substitution product may be obtained with excellent selectivity.[2]

During the past decades a plethora of chiral ligands has been investigated in asymmetric allylic substitution reactions although only some of them have been recognized as "privileged ligands", according to the definition given by Jacobsen.[3] In bidentate ligands containing two different donor atoms the *trans* effect exerted by the strong σ-donor atom plays a determining role in the enantiodiscrimination process,[4] as well established by the privileged family of PHOX ligands;[5] on the other hand, steric effects prevail over electronic effects in homo bidentate ligands. In contrast to *P*,*P*-ligands,[6] which are extremely useful in asymmetric hydrogenation reactions, dinitrogen ligands are successfully and frequently employed in allylic substitution reactions. In particular, C_2-symmetric chelating ligands[7] have been proven to possess the requirements for inducing high enantioselectivity since they reduce the number of possible transition states that compete in the enantiomeric enrichment process.

In previous work[8] we have investigated the use of C_1-symmetric dinitrogen chiral ligands featuring a binaphthylazepine moiety, and which differed in the scaffold rigidity of the achiral portion, which were a 2-picolyl or 8-quinolinyl group. In this study we found that the formation of a flexible five-membered palladacycle favours the activity and enantioselectivity of the catalyst, with *ee* values up to 82% in the allylic alkylation of *rac*-1-acetoxy-1,3-diphenylpropene. The same ligands were applied in the ruthenium-catalyzed allylic alkylation and etherification of cinnamyl derivatives, which are prototypes of unsymmetrical allylic substrates, and the synthesized precalysts led to high regioselectivity towards the branched product and moderate *ee* values.[9]

Following our studies of palladium-catalyzed allylic alkylation reactions with symmetrical substrates, we have designed new bidentate C_1-symmetric ligands exploiting the benefits of several structural elements: (a) a binaphthylazepine group along with either a bornyl fragment as

[a] Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica-Fisica dell'Università di Messina,
Salita Sperone 31, Vill. S. Agata, 98166 Messina, Italy
[‡] Current address: Instituto de Investigaciones Químicas,
Consejo Superior de Investigaciones Científicas and
Universidad de Sevilla,
Avenida Américo Vespucio no. 49, Isla de la Cartuja,
41092 Sevilla, Spain
E-mail: giovanni.bottari@iiq.csic.es
[‡‡] Current address: Dipartimento di Scienze Chimiche,
Università di Trieste,
Via Licio Giorgieri 1, 34127 Trieste, Italy
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100113.

further source of chirality[10] or a simple NMe_2 group; (b) the flexibility of the catalyst metallacycle is ensured by the presence of an ethylenic spacer between the donor atoms, with the consequential formation of a stable five-membered ring; (c) the electronic differentiation of the donor atoms was ensured by use of two ligand typologies, namely, diamines and mixed amine-imine ligands. Furthermore, this study also involved the synthesis of analogue ligands featuring only a bornyl fragment as the chiral source and an NMe_2 group, as well as the investigation of the coordination chemistry of selected palladium complexes, and the catalytic application of these complexes in palladium-catalyzed allylic substitution reactions.

Results and Discussion

Synthesis of Ligands

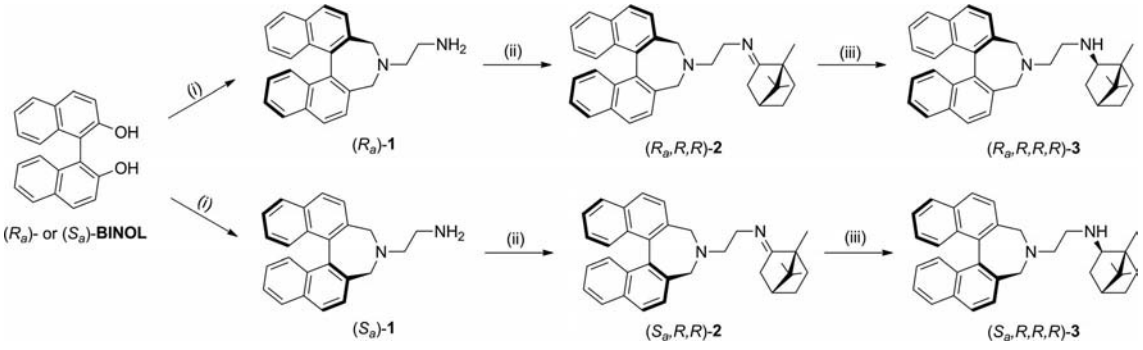
The synthesis of ligands featuring the binaphthylazepine moiety started from (R_a)- or (S_a)-1,1′-binaphthol, which can be converted easily into the compounds (R_a)-**1** or (S_a)-**1** after four synthetic steps, according to the literature.[7f,11]

The reaction between the NH_2 group of the enantiomeric diamines (R_a)-**1** and (S_a)-**1** and the (*R*)-(+)-camphor carbonyl group, in refluxing toluene in the presence of catalytic amounts of *p*-toluenesulfonic acid afforded the desired diastereomeric amine-imine ligands (R_a,*R*,*R*)-**2** and (S_a,*R*,*R*)-**2**, as depicted in the Scheme 1, in good yields. The subsequent reduction of the C=N bond within (R_a,*R*,*R*)-**2** and (S_a,*R*,*R*)-**2** with sodium borohydride and nickel chloride readily gave the new diamine ligands (R_a,*R*,*R*,*R*)-**3** and (S_a,*R*,*R*,*R*)-**3**.[10c]

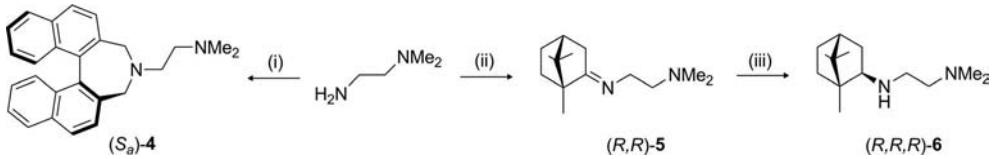
It is clear that the reduction involves the formation of a stereogenic carbon atom and two possible diastereomers are expected. However, only one diastereomer was detected by ^1H NMR and the absolute configuration of the stereogenic centre (*R*)[10f] was determined by means of multidimensional NMR techniques.

In order to evaluate the different asymmetry induction effects of the chiral binaphthylazepine and bornyl moieties in catalytic experiments, *N*,*N* ligands (S_a)-**4**, (*R*,*R*)-**5** and (*R*,*R*,*R*)-**6** in which one of the two chiral arms present in the diastereomeric ligand pairs **2** and **3** were replaced by a simple achiral NMe_2 group, were synthesized according to the Scheme 2. Ligand (S_a)-**4** was reported for the first time by Cram and co-workers,[12] who used it as chiral controller in the asymmetric addition of alkyllithium reagents to aldehydes. Some years later this ligand was used by Rosini and co-workers[13] in the enantioselective dihydroxylation of olefins; to the best of our knowledge no data related to its use in palladium-catalyzed allylic substitution are present in literature. Ligand (*R*,*R*)-**5** was obtained by a condensation reaction between (*R*)-(+)-camphor and *N*,*N*-dimethylethylenediamine. The reduction of the C=N double bond in (*R*,*R*)-**5** gave (*R*,*R*,*R*)-**6** as the major isomer, while traces of the corresponding diastereomer with *S* configuration at the new stereogenic carbon atom were revealed by GC–MS. Although the complete removal of the minor diastereomer was not successful, it is reasonable to neglect its effect in subsequent studies. All ligands were fully characterized by NMR spectroscopy and elemental analysis; they are stable in air and even the amine-imine ligands are resistant to hydrolysis.

From a general point of view, the two arms of the ligands produce sterically differentiated environments, especially in ligands (S_a)-**4**, (*R*,*R*)-**5** and (*R*,*R*,*R*)-**6** that contain a small NMe_2 fragment and a bulkier binaphthylazepine or bornyl chiral arm.



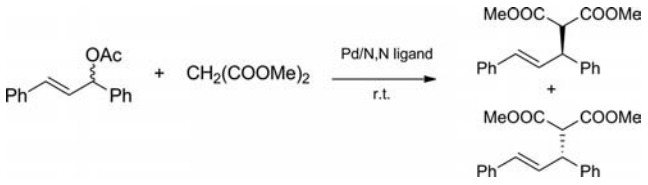
Scheme 1. Reagents and conditions: (i) See ref.[7f]; (ii) (*R*)-(+)-camphor, PTSA (*p*-toluenesulfonic acid), toluene, Dean–Stark conditions; (iii) $NaBH_4$, $NiCl_2$, MeOH, –40 °C to room temp.



Scheme 2. Reagents and conditions: (i) (S_a)-2,2′-dibromomethyl-1,1′-binaphthalene, toluene, 65 °C; (ii) (*R*)-camphor, PTSA, toluene, Dean–Stark conditions; (iii) $NaBH_4$, $NiCl_2$, MeOH, –40 °C to room temp.

Catalytic Experiments

The synthesized chiral *N*,*N*-ligands were evaluated in the allylic alkylation reaction of *rac*-1-acetoxy-1,3-diphenylpropene with dimethyl malonate under Trost conditions (Scheme 3). The active species was formed in situ by mixing $[Pd(\eta^3\text{-allyl})Cl]_2$ and the *N*,*N*-ligand in an 1:2.2 ratio in an appropriate solvent, and the results from these reactions are reported in Table 1.



Scheme 3. Allylic alkylation reaction of *rac*-1-acetoxy-1,3-diphenylpropene catalyzed by Pd/*N*,*N*-catalysts.

Table 1. Details of the palladium-catalyzed allylic alkylation reactions of *rac*-1-acetoxy-1,3-diphenylpropene.[a]

Entry	*N*,*N*-ligand	Yield [%][b]	*ee* [%][c]
1	(R_a,*R*,*R*)-**2**	12	68 (*S*)
2	(S_a,*R*,*R*)-**2**	18	76 (*S*)
3	(R_a,*R*,*R*,*R*)-**3**	84	98 (*S*)
4[d,e]	(R_a,*R*,*R*,*R*)-**3**	>99	>99 (*S*)
5	(S_a,*R*,*R*,*R*)-**3**	16	92 (*S*)
6[d]	(S_a,*R*,*R*,*R*)-**3**	38	96 (*S*)
7[e]	(S_a)-**4**	>99	95 (*S*)
8	(*R*,*R*)-**5**	15	66 (S)
9	(*R*,*R*,*R*)-**6**	26	55 (*S*)

[a] Experimental conditions: $[Pd(\eta^3\text{-allyl})Cl]_2$/*N*,*N*-ligand/substrate/dimethyl malonate/BSA [bis(trimethylsilyl)acetamide] = 1:2.2:100:300:300, in CH_2Cl_2 (if not stated otherwise), a pinch of KOAc, room temp., 16 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by chiral HPLC (see experimental section for details). [d] The catalytic run was carried out in toluene instead of CH_2Cl_2. [e] Complete conversion was observed after 4 h.

The catalytic systems showed poor to excellent activity in the catalytic tests, with the Pd/(R_a,*R*,*R*,*R*)-**3** and Pd/(S_a)-**4** complexes being the most efficient catalysts in terms of both product yield and enantioselectivity; in fact, the reaction involving Pd/(R_a,*R*,*R*,*R*)-**3** was complete in about 4 h (as monitored by GC–MS) with *ee* values of >99% (Table 1, entry 4). The solvent does have an influence on the catalytic results and changing from dichloromethane to the less polar toluene gives a moderate increase in the conversion and a slight improvement of asymmetric induction when ligands (R_a,*R*,*R*,*R*)-**3** and (S_a,*R*,*R*,*R*)-**3** were used, as clearly highlighted by comparison between entries 3 and 4, and entries 5 and 6, in Table 1. It was not possible to verify if this trend applies to ligand (S_a)-**4** due to the precipitation of the active species Pd/(S_a)-**4** when formed in toluene. The palladium catalysts containing mixed amine-imine ligands, (R_a,*R*,*R*)-**2**, (S_a,*R*,*R*)-**2** and (*R*,*R*)-**5**, gave only low conversion levels, although the enantioselectivity of (S_a,*R*,*R*)-**2** was good (up to 76%, entry 2, Table 1); it is likely that the catalytic activity of these complexes is suppressed by the rigidity of the iminic moiety coordination.

Interestingly, bornyl and binaphthylazepine chiral arms in ligands (S_a,*R*,*R*,*R*)-**3** and (R_a,*R*,*R*,*R*)-**3** play a synergic role in inducing high enantiomeric excesses, and only a small mismatching effect can be ascribed to the catalysts containing these ligands, which differ in the absolute configuration of the atropisomeric binaphthyl moiety. It is also noteworthy that the structurally simple and easily accessible ligand (S_a)-**4** is able to induce 95% *ee* under standard allylic alkylation conditions. In Figure 1 our best results are compared to that obtained by Moberg and co-workers with a C_2-symmetric binaphthylazepine-based dinitrogen ligand.

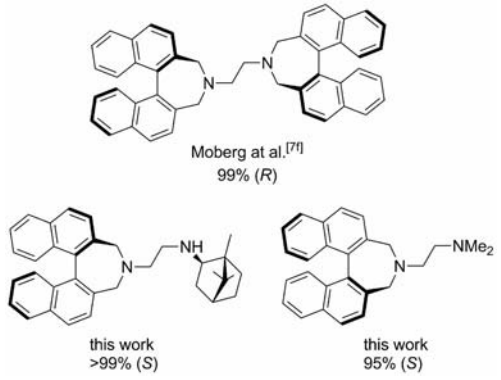
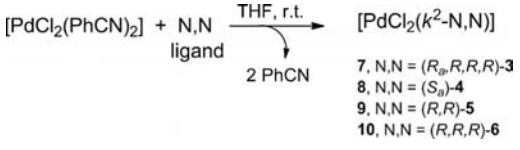


Figure 1. Comparison of *ee* values obtained in this work with that reported by Moberg using a C_2-symmetric ligand.[7f]

The ligands in Figure 1 contain binaphthylazepine groups and form flexible five-membered palladacycles, which shows that the symmetry of the ligand is not a factor that dramatically influences the selectivity of the catalytic process. However, the presence of the binaphthylazepine moieties is beneficial in the enantiocontrol process. Finally, it appears that when in presence of the mixed ligand pairs **2** and **3** the absolute configuration of the substitution product is determined by the chirality of the bornyl moiety, which always assumes the descriptors (*R*,*R*) or (*R*,*R*,*R*), while compounds containing a binaphthylazepine group afforded the *S* product regardless of the absolute configuration of this group, which can be either R_a or S_a.

Coordination Chemistry and Solution Studies

The reactions between $[PdCl_2(PhCN)_2]$ and some selected *N*,*N*-ligands were investigated in order to evaluate the coordination modes and spatial arrangement of the coordinated ligands. The reactions were carried out with a Pd/*N*,*N*-ligand ratio of 1:1.2, in THF, at room temperature, and the mixture was left to react for 2 h, in accordance with the equation in Scheme 4.

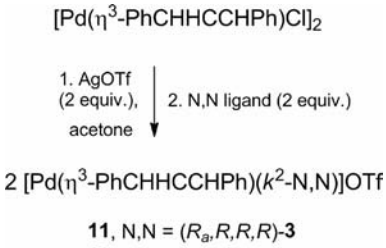


Scheme 4. Synthesis of $[PdCl_2(k^2\text{-}N,N\text{-ligand})]$ complexes.

All the synthesized complexes were fully characterized by NMR and elemental analysis. Although we did not obtain

suitable crystals for X-ray diffraction analysis, NMR analysis revealed a bidentate coordination mode for the *N*,*N*-ligands with palladium. In the ^{1}H NMR spectrum of compound **7** [$PdCl_2${(R_a,*R*,*R*,*R*)-**3**}] a shift of the proton signals of the *N*,*N*-ligand relative to the signals of the uncoordinated ligand was observed; for instance, the AB system attributed to the azepinic CH_2 groups of the free ligand turns into four doublets in the spectrum of **7**, and one methylenic group of the coordinated ligand experiences the proximity of the palladium centre and gives two well resolved doublets at δ = 4.80 and 2.90 ppm in the spectrum of **7**. The ethylenic spacer protons show signals between δ = 4.37 and 2.25 ppm, while the NH signal in the spectrum of **7** is shifted significantly downfield with respect to the same signal in the spectrum of the free ligand (broad singlet at δ = 6.25 ppm compared to 1.72 ppm in the free ligand spectrum). The coordination of the NMe_2 containing ligands, (S_a)-**4**, (*R*,*R*,*R*)-**5** and (*R*,*R*,*R*)-**6**, to palladium was witnessed by the appearance of two different singlets (in the 2–3 ppm range) in the spectra of their coordination complexes that arise due to the diastereotopicity of the methyl groups after the chelation process, which is in contrast to the unique singlet in ^{1}H NMR spectra of the corresponding free ligands. Also, the C=N carbon atom of (*R*,*R*,*R*)-**6** is strongly shifted downfield in the ^{13}C NMR spectrum of the coordinated ligand (δ = 196.9 ppm compared to 182.4 ppm in spectrum of the free ligand), confirming that the iminic nitrogen atom is bonded to the metal centre.

As shown in Scheme 5, we have also prepared the palladium allyl complexes containing ligands (S_a)-**4** and (R_a,*R*,*R*,*R*)-**3**, which showed the best catalytic performance out of all the complexes reported herein.



Scheme 5. Synthesis of palladium allyl complexes.

NMR analysis of the allylic complexes {[Pd(R_a,*R*,*R*,*R*)-**3**][(η^3-PhCHCHCHPh)]OTf} (**11**) and {[Pd{(S_a)-**4**}(η^3-PhCHCHCHPh)]OTf} (**12**) gave useful information about the catalytic active species formed in solution. For complex **11**, ^{1}H NMR spectra revealed the presence of two conformational allylic isomers in a 75:25 ratio; in both species, 2D NOESY spectroscopy indicates a *syn*-*syn* arrangement for the phenyl substituents on the allylic fragment with respect to the central allylic hydrogen, and both isomers are in equilibrium. In Figure 2 (a) the two isomers are illustrated, and can be called *exo*-*syn*-*syn* and *anti*-*syn*-*syn*, in accordance to the nomenclature proposed by Widhalm and coworkers.[14] In previous work,[8] we correlated the observed enantiomeric excess with the concentration of the allylic species, and with their reactivity under equilibrium conditions. In order to explain the high enantioselectivity of this complex, a complete structural assignment of the allylic species would be advantageous. Unfortunately, due the complexity of the NMR spectra of complex **11**, it was necessary for us to limit the study to the relationship between the palladium-allyl species and the origin of enantioselectivity of the "model" complex **12**. This complex is also present in solution as a mixture of two *syn*-*syn* isomers, which do not undergo exchange processes, in a ratio of ca. 96:4. On the basis of the NOE crosspeaks between the allylic moiety and the ligand (Figure 2, a), an *endo*-*syn*-*syn* conformation was assigned to the major isomer, and as this is the only species contributing to the enantioenrichment, since no exchange processes are observed, the *S* configuration of the product can be explained by the nucleophilic attack at the allylic carbon *trans* to the binaphthylazepine group affording the corresponding (η^2-olefinic)palladium species (Figure 2, b); in this case, the olefin rotation should not be affected by possible interactions with the binaphthylazepine group.

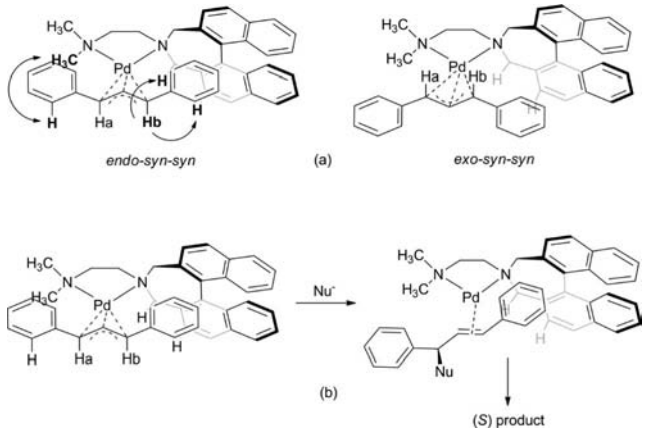


Figure 2. (a) Allylic conformers of complex [Pd{(S_a)-**4**}(η^3-PhCHHCCHPh)]OTf in $CDCl_3$ solution, also shown are some selected NOE contacts within the major isomer (the OTf anion is omitted for clarity). (b) Formation of the (*S*) substitution product from the nucleophilic attack at the C-Ha carbon atom of the *endo*-*syn*-*syn* isomer (the OTf anion is omitted for clarity).

Indeed, the enantiomeric ratio of the product (97.5:2.5, as determined by chiral HPLC; see Table 1, entry 7) is consistent with the observed ratio of the palladium-allyl conformational isomers in solution, 96:4, as determined by ^{1}H NMR integration of allylic proton signals. The small difference in these ratios is attributable to the measurement method and the experimental conditions of the catalytic test with respect to those of the complex analysis, particularly the differences in the counteranion and solvent. The basicity properties of both nitrogen atoms are very similar as reflected in the close chemical shift values of the C1 and C3 allylic carbon atoms in the ^{13}C NMR spectrum of complex **12** (75.4 and 78.9 ppm, respectively), this is due to a comparable *trans* influence of the donor atoms. On the other hand, it is reasonable to assume that steric effects must play a role in determining the high enantioselectivity

of this complex, with the bulky binaphthylazepine group exerting an excellent degree of regio- and, more specifically, enantio-control.

An analogous regioselectivity in the nucleophilic attack of complex **11** is possible, since the *trans*-effect of the NH nitrogen atom is slightly lower than that of the tertiary nitrogen atom, and an *endo-syn-syn* conformation is expected for the more reactive allylic species in order to explain the *S* configuration of the product. Apart from these weak electronic effects, the low number of conformational isomers, along with the cooperative steric effects of the binaphthylazepine and bornyl groups in the ligand (R_a,*R*,*R*,*R*)-**3** are definitively crucial in determining the very high enantiomeric excess of products arising from reactions involving this ligand.

Conclusions

In conclusion, we have synthesized a new family of dinitrogen ligands containing both a binaphthylazepine and a bornyl group, which are derived from (*R*)-(+)-camphor and have a flexible ethylenic spacer between the nitrogen donor atoms. The evaluation of the individual effects of the different ligand components on the product chirality was made possible by comparison of the catalytic performance of these ligands with those of ligands containing only one chiral arm, either a binaphthylazepine or a bornyl fragment, with the second arm being replaced with an achiral NMe_2 group. The ligands featuring sp^2 and sp^3 nitrogen atoms, which can rely on a strong *trans* effect of the iminic nitrogen to create an electronic differentiation between the two allylic carbon atoms, produced lower *ee* values than diamine ligands, whose donor atoms possess a nearly equal basicity, when employed in allylic alkylation reactions. On the other hand, it seems that steric effects play a dominant role in the catalytic process, especially when the coordinated ligand contains a binaphthylazepine moiety that is remarkably bulky. As a result, although a synergic effect between the two chiral arms was observed in the diastereomer (R_a,*R*,*R*,*R*)-**3**, which afforded a >99% *ee* in the allylic alkylation of *rac*-1,3-diphenylacetoxy-1-propene, it seems that the binaphthylazepine backbone possesses an intrinsic capability to exhibit enantiocontrol in this reaction since a 95% *ee* was reached when the palladium complex containing ligand (S_a)-**4** was used, even though the bornyl group was replaced with an achiral fragment in this ligand. In principle, the functionalization of the aminic group in the precursor **1** with different chiral derivatives, or achiral fragments, with different steric demands, could be exploited to improve the catalytic performance of palladium complexes of this class of ligand, and to extend their applicability in the allylic alkylation of a broad range of substrates. The potential of this new class of ligands as possible components in catalysts resides in the possibility of modulating their structures inexpensively.

The NMR study of allyl palladium complexes containing ligands (R_a,*R*,*R*,*R*)-**3** and (S_a)-**4** revealed the presence in solution of two allylic isomers. Furthermore, these complexes gave excellent *ee* values when used as catalysts in allylic alkylation reactions, and in one case (Table 1, entry 4), slightly better catalytic results were obtained than the best results reported in the literature for related dinitrogen ligands.[7f] In one case, the characterization of the isomers and their ratio in solution, along with the identification of exchange processes in solution, were found to be correlated strongly with the observed enantiomeric excess when the complex was used to catalyze allylic alkylation reactions. Finally, this work highlights the capability of stable and easily available phosphane-free ligands to form highly selective catalysts for allylic substitution reactions, which is in contrast to the extensive literature related to the use of chiral *P*,*N*- or *P*,*P*-ligands in such reactions.[15]

Experimental Section

General Methods: All manipulations involving air-sensitive chemicals were performed in argon or nitrogen atmospheres. Solvents were dried and distilled prior to use according to standard procedures. (S_a)-(+)-2,2′-dibromomethyl-1,1′-binaphthalene and (S_a)-2-(3H-dinaphtho[2,1-c:1′,2′-e]azepin-4(5*H*)-yl)ethanamine were synthesized according to a literature procedure.[7f] All other reagents were purchased from Sigma–Aldrich and Strem and used as supplied. For column chromatography, silica gel 60 (220 ± 440 mesh) purchased from Fluka, and basic alumina (70–290 mesh) from Aldrich, were used. 1D and 2D NMR experiments were carried out with a 500 MHz Varian or 300 MHz Bruker spectrometers. Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano. Enantiomeric excesses were determined by chiral HPLC with a Chiralcel OD-column, and the absolute configuration of the materials were determined by comparison with reported data.

Synthesis of Ligands

(*E*)-2-{(R_a)-3*H*-Dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-yl}-*N*-{(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene}ethanamine [(R_a,*R*,*R*)-2] and (*E*)-2-{(S_a)-3*H*-Dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-yl}-*N*-{(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene}ethanamine [(S_a,*R*,*R*)-2]: In a 10 mL one-neck flask (*R*)- or (*S*)-**1** (0.726 g, 2.15 mmol), (*R*)-(+)-camphor (0.345 g, 2.27 mmol) and *p*-toluenesulfonic acid (22 mg, 0.11 mmol) were dissolved in 2 mL of anhydrous toluene. The reaction mixture was vigorously stirred overnight, under reflux conditions, in a Dean–Stark apparatus. The progress of the reaction was monitored by TLC, and after no trace of the starting amine was detected, the solution was cooled down and the solvent evaporated under reduced pressure to give the corresponding crude imine.

(R_a,*R*,*R*)-2: This material was purified by chromatography (basic alumina, toluene:ethyl acetate, 15:1). Pale yellow solid; yield 750 (74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3), 1.20 (m, 1 H), 1.38 (m, 1 H), 1.69 (m, 1 H), 1.78–2.01 (m, 3 H), 2.36–2.50 (m, 1 H), 2.65 (m, 1 H), 2.94 (m, 1 H), 3.38–3.64 (m, 2 H), 3.79 and 3.24 (AB, J = 12 Hz, 4 H, 2× ArCH_2N), 7.27 (m, 2 H), 7.47 (m, 4 H), 7.62 (d, J = 8 Hz, 2 H), 7.95 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.5 (*C*H_3), 19.0 (*C*H_3), 19.5 (*C*H_3), 27.4 (*C*H_2), 32.1 (*C*H_2), 35.8 (*C*H_2), 43.8 (*C*H), 47.0 (*C*), 51.8 (*C*H_2), 53.7 (*C*), 55.6 (*C*H_2), 55.7 (*C*H_2), 125.3 (*C*H Ar), 125.6 (*C*H Ar), 127.4 (*C*H Ar), 127.9 (*C*H Ar), 128.2 (*C*H Ar), 131.3 (*C* Ar), 133.1 (*C* Ar), 133. 6 (*C*

Ar), 134.9 (*C* Ar), 182.9 (*C*=N) ppm. $C_{34}H_{36}N_2$ (472.67): calcd. C 86.40, H 7.68, N 5.93; found C 86.58, H 7.52, N 5.90.

(S_a,*R*,*R*)-2: This material was purified by chromatography (basic alumina, toluene:ethyl acetate, 15:1). Pale yellow solid; yield 640 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3), 1.00 (s, 3 H, CH_3), 1.15–1.24 (m, 1 H), 1.32–1.42 (m, 1 H), 1.61–1.94 (m, 3 H), 2.33–2.43 (m, 1 H), 2.62 (dt, *J* = 12 and 7 Hz, 1 H), 2.92 (dt, *J* = 12 and 7 Hz, 1 H), 3.50 (t, *J* = 7 Hz, 2 H, C=NCH_2), 3.77 and 3.24 (AB, *J* = 12 Hz, 4 H, 2× ArCH_2N), 7.23–7.39 (m, 2 H), 7.42–7.50 (m, 4 H), 7.60 (d, *J* = 9 Hz, 2 H), 7.95 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.5 (*C*H_3), 19.0 (*C*H_3), 19.6 (*C*H_3), 27.5 (*C*H_2), 32.1 (*C*H_2), 35.8 (*C*H_2), 43.8 (*C*H), 47.1 (*C*), 51.7 (*C*H_2), 53.6 (*C*), 55.5 (*C*H_2), 55.6 (*C*H_2), 125.3 (*C*H Ar), 125.7 (*C*H Ar), 127.4 (*C*H Ar), 127.9 (*C*H Ar), 128.3 (*C*H Ar), 131.3 (*C* Ar), 133.1 (*C* Ar), 133.6 (*C* Ar), 135.0 (*C* Ar), 175.7 (*C*=N) ppm. $C_{34}H_{36}N_2$ (472.67): calcd. C 86.48, H 7.58, N 5.93; found C 86.55, H 7.51, N 5.94.

(S_a)-2-{3*H*-Dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-yl}-*N*,*N*-dimethylethanamine [(S_a)-4]: In a Schlenk flask under argon, (S_a)-2,2′-dibromomethyl-1,1′-binaphthalene (440 mg, 1 mmol) and *N*,*N*-dimethylethylenediamine (2 mL) were dissolved in toluene (5 mL) and the solution was left stirring overnight at 60 °C. Water (25 mL) and diethyl ether (25 mL) were then added and the organic phase collected, dried with $MgSO_4$, filtered and concentrated under reduced pressure. The product was used without further purification; yield 340 mg (93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 6 H, 2× NCH_3), 2.54 (m, 3 H), 2.74 (m, 1 H), 3.72 and 3.21 (AB, *J* = 12 Hz, 4 H, 2× ArCH_2N), 7.25 (m, 2 H), 7.46 (m, 4 H), 7.56 (d, *J* = 8 Hz, 2 H), 7.93 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.0 (2× *C*H_3), 53.3 (*C*H_2), 55.7 (*C*H_2), 58.0 (2× *C*H_2), 125.3 (*C*H Ar), 125.7 (*C*H Ar), 127.4 (*C*H Ar), 127.8 (*C*H Ar), 128.2 (*C*H Ar), 131.3 (*C* Ar), 133.1 (*C* Ar), 133.4 (*C* Ar), 134.9 (*C* Ar) ppm. $C_{26}H_{26}N_2$ (366.50): calcd. C 85.21, H 7.15, N 7.64; found C 84.98, H 7.35, N 7.67.

(*E*)-N^1,N^1-Dimethyl-N^2-{(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]-heptan-2-ylidene}ethane-1,2-diamine [(*R*,*R*)-5]: (*R*)-(+)-camphor (3 mmol, 456 mg) and *N*,*N*-dimethylethylenediamine (2 mL) were dissolved in anhydrous toluene (2 mL) and the solution was heated under reflux in a Dean–Stark trap. The reaction was monitored by GC–MS and after the camphor was completely consumed, the mixture was cooled to room temperature. The excess of *N*,*N*-dimethylethylenediamine was removed under vacuum and the imine was obtained in high purity as pale yellow oil; yield 652 mg (98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3), 1.18 (m, 1 H), 1.33 (m, 1 H), 1.64 (m, 1 H), 1.77–1.89 (m, 2 H), 1.92 (t, *J* = 4 Hz, 1 H), 2.27 (s, 6 H, 2× CH_3), 2.34 (m, 1 H), 2.52 (t, *J* = 8 Hz, 2 H), 3.33 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.4 (*C*H_3), 18.9 (*C*H_3), 19.5 (*C*H_3), 27.4 (*C*H_2), 32.1 (*C*H_2), 35.5 (*C*H_2), 43.8 (*C*H), 45.9 (2× N*C*H_3), 47.0 (*C*), 50.9 (C=N*C*H_2), 53.5 (*C*), 59.9 [$(CH_3)_2$N*C*H_2], 182.9 (*C*=N) ppm. $C_{14}H_{26}N_2$ (222.37): calcd. C 75.62, H 11.79, N 12.60; found C 75.53, H 11.98, N 12.49.

General Procedure for Imine Reduction: In a three-necked flask equipped with a bubbler, the imine (1 equiv.) was dissolved in a mixture of anhydrous methanol and chloroform (4:1). To this solution, anhydrous $NiCl_2$ (2.1 equiv.) was added, the flask was cooled to –40 °C and $NaBH_4$ (3.1 equiv.) was added in portions over a period of 1 h. The reaction mixture was left stirring overnight at room temperature. The excess of $NaBH_4$ was quenched with an aqueous solution of 5% NaOH and the product extracted three times in a separation funnel with chloroform. The organic phase was washed with brine, dried ($MgSO_4$) and concentrated under vacuum to give the crude amine.

(1*R*,2*R*,4*R*)-*N*-[2-{(R_a)-3*H*-Dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-yl}ethyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine [(R_a,*R*,*R*,*R*)-3]: This compound was purified by chromatography (silica, pentane:ethyl acetate, 3:1, 2% methanol). White solid; yield 92%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82 (s, 3 H, CH_3), 0.90 (s, 3 H, CH_3), 1.01–1.11 (m, 4 H), 1.48–1.74 (m, 6 H), 2.44–2.57 (m, 3 H), 2.67–2.81 (m, 3 H), 3.70 and 3.18 (AB, *J* = 12 Hz, 4 H, 2× ArCH_2N), 7.23–7.28 (m, 2 H), 7.42–7.49 (m, 4 H), 7.54 (d, *J* = 8 Hz, 2 H), 7.94 (d, *J* = 8 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.3 (*C*H_3), 20.5 (*C*H_3), 20.6 (*C*H_3), 27.4 (*C*H_2), 37.0 (*C*H_2), 39.1 (*C*H_2), 45.3 (*C*H), 46.3 (*C*H_2), 46.7 (*C*H_2), 47.1 (*C*H_2), 48.5 (*C*H_2), 55.1 (*C*H_2), 55.5 (*C*H_2), 67.2 (*C*H), 125.5 (*C*H Ar), 125.7 (*C*H Ar), 127.5 (*C*H Ar), 127.8 (*C*H Ar), 128.2 (*C*H Ar), 128.3 (*C*H Ar), 131.4 (*C* Ar), 133.1 (*C* Ar), 133.8 (*C* Ar), 135.0 (*C* Ar) ppm. $C_{34}H_{38}N_2$ (474.69): calcd. C 86.03, H 8.07, N 5.90; found C 86.21, H 7.83, N 5.96.

(1*R*,2*R*,4*R*)-*N*-[2-{(S_a)-3*H*-Dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-yl}ethyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine [(S_a,*R*,*R*,*R*)-3]: This compound was purified by chromatography (silica, pentane:ethyl acetate, 3:1, 5% methanol). White solid; yield 87%. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.85 (s, 3 H, CH_3), 1.03 (s, 3 H, CH_3), 1.08–1.20 (m, 3 H), 1.28 (s, 3 H, CH_3), 1.45–1.78 (m, 6 H), 2.39–2.48 (m, 1 H), 2.53–2.62 (m, 2 H), 2.66–2.81 (m, 2 H), 3.51 and 3.18 (AB, *J* = 12 Hz, 4 H, 2× ArCH_2N), 6.97–7.04 (m, 2 H), 7.17–7.24 (m, 2 H), 7.60–7.71 (m, 4 H), 7.34 (d, *J* = 8 Hz, 2 H), 7.64 (d, *J* = 8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 12.5 (*C*H_3), 20.9 (*C*H_3), 27.9 (*C*H_2), 37.3 (*C*H_2), 39.4 (*C*H_2), 45.8 (*C*H), 47.0 (*C*H_2), 47.2 (*C*H_2), 48.8 (*C*H_2), 55.6 (*C*H_2), 55.8 (*C*H_2), 67.9 (*C*H), 125.7 (*C*H Ar), 126.1 (*C*H Ar), 127.9 (*C*H Ar), 128.1 (*C*H Ar), 128.5 (*C*H Ar), 128.6 (*C*H Ar), 132.0 (*C* Ar), 133.7 (*C* Ar), 134.4 (*C* Ar), 135.5 (*C* Ar) ppm. $C_{34}H_{38}N_2$ (474.69): calcd. C 86.03, H 8.07, N 5.90; found C 86.46, H 7.78, N 5.76.

N^1,N^1-Dimethyl-N^2-{(1*R*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]-heptan-2-yl}ethane-1,2-diamine [(R_a,*R*,*R*)-6]: Colourless oil; yield 89%. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.92 (s, 3 H, CH_3), 1.06 (s, 3 H, CH_3), 1.18 (m, 2 H), 1.35 (s, 3 H, CH_3), 1.56–1.70 (m, 2 H), 1.77 (m, 3 H), 2.15 (s, 6 H, 2× NCH_3), 2.25–2.48 (m, 2 H), 2.60 (m, 2 H), 2.72 (m, 1 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 12.3 (*C*H_3), 20.8 (2× *C*H_3), 27.8 (*C*H_2), 37.1 (*C*H_2), 39.1 (*C*H_2), 45.3 (2× N*C*H_3), 45.7 (*C*H), 46.8 (*C*H_2), 48.6 (*C*), 59.5 (*C*H_2), 67.7 (*C*HNH) ppm. $C_{14}H_{28}N_2$ (224.39): calcd. C 74.94, H 12.58, N 12.48; found C 75.05, H 12.50, N 12.45.

Synthesis of Palladium Complexes

[$PdCl_2${(R_a,*R*,*R*,*R*)-3}] (7): In a two-neck flask containing a solution of [$Pd(PhCN)_2Cl_2$] (54 mg, 0.14 mmol) in THF (5 mL), a solution of ligand (R_a,*R*,*R*,*R*)-**3** (38 mg, 0.08 mmol) in the same solvent (5 mL) was added. After stirring for 2 h the solvent was removed by evaporation and the residue was dissolved in the minimum amount of dichloromethane and filtered through celite; after adding pentane (25 mL) a yellow powder was obtained. The resulting solid was washed several times with pentane, and then dried under vacuum; yield 35 mg (71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (s, 3 H, CH_3), 0.85 (s, 3 H, CH_3), 1.07 (s, 3 H), 1.16–1.50 (m, 3 H), 1.78 (m, 1 H), 1.86 (m, 1 H, C*H*), 2.13 (m, 1 H), 2.22–2.36 (m, 3 H), 2.86 (m, 1 H), 4.16 (bt, 1 H, CH_2NHC*H*), 4.37 (dt, *J* = 12 and 3 Hz, 1 H, C$H_2$$CH_2$NH), 4.66 and 4.59 (AB, *J* = 12 Hz, 2 H, ArCH_2N), 4.81 and 2.92 (AB, *J* = 12 Hz, 2 H, ArC′H_2N), 6.26 (br. s, 1 H, N*H*), 7.12–7.27 (m, 3 H), 7.38–7.46 (m, 3 H), 7.55 (d, *J* = 8 Hz, 1 H), 7.69 (d, *J* = 8 Hz, 1 H), 7.81 (d, *J* = 8 Hz, 1 H), 7.97 (d, *J* = 8 Hz, 1 H), 8.08 (d, *J* = 8 Hz, 1 H), 8.25 (d, *J* = 8 Hz, 1 H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9 (*C*H$_3$), 21.5 (*C*H$_3$), 22.0 (*C*H$_3$), 26.4 (*C*H$_2$), 32.9 (*C*H$_2$), 39.6 (*C*H$_2$), 44.5 (*C*H), 45.4 (*C*H$_2$), 46.8 (*C*), 50.9 (*C*), 60.4 (*C*H$_2$), 62.5 (*C*H$_2$), 63.1 (*C*H$_2$), 68.6 (*C*H), 125.6 (*C*H Ar), 125.8 (*C*H Ar), 125.9 (*C*H Ar), 126.0 (*C*H Ar), 127.50 (*C*H Ar), 127.52 (*C*H Ar), 128.3 (*C*H Ar), 128.38 (*C*H Ar), 128.4 (*C*H Ar), 128.7 (*C*H Ar), 129.2 (*C*H Ar), 131.0 (*C* Ar), 130.2 (*C*H Ar), 131.08 (*C*H Ar), 131.1 (*C*H Ar), 131.2 (*C*H Ar), 133.4 (*C*H Ar), 133.9 (*C*H Ar), 135.2 (*C*H Ar), 136.2 (*C*H Ar) ppm. $C_{34}H_{37}Cl_2N_2Pd$ (650.99): calcd. C 62.73, H 5.73, N 4.30; found C 62.82, H 5.81, N 4.23.

[PdCl$_2${(S_a)-4}] (8): This complex was synthesized according to the same procedure reported for **7**; yield 88%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (m, 2 H, C*H*$_2$NMe$_2$), 2.89 (s, 3 H, NC*H*$_3$), 2.94 [m, 1 H, C*H*$_2$CH$_2$N(CH$_3$)$_2$], 2.99 (s, 3 H, NC*H*$_3$), 3.04 (d, *J* = 11.8 Hz, 1 H, C*H*$_2$), 3.83 (d, *J* = 13.8 Hz, 1 H, C*H*$_2$), 4.90 (d, *J* = 13.8 Hz, 1 H, C*H*$_2$), 4.91 (d, *J* = 11.8 Hz, 1 H, C*H*$_2$), 7.20–7.36 (m, 3 H, *H* Ar), 7.35–7.57 (m, 4 H, *H* Ar), 7.95–8.00 (m, 3 H, *H* Ar), 8.03 (d, *J* = 8.4 Hz, 1 H, *H* Ar), 8.18 (d, *J* = 8.4 Hz, 1 H, *H* Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.6 (N*C*H$_3$), 53.3 (N*C*′H$_3$), 61.3 (N*C*H$_2$CH$_2$N), 61.9 (N*C*′H$_2$CH$_2$N), 62.3 (Ar*C*H$_2$N), 62.9 (Ar*C*′H$_2$N), 125.9 (*C*H Ar), 126.2 (*C*H Ar), 126.5 (*C*H Ar), 126.6 (*C*H Ar), 127.3 (*C*H Ar), 127.8 (*C*H Ar), 127.9 (*C*H Ar),128.3 (*C*H Ar), 128.6 (*C*H Ar), 128.7 (*C*H Ar), 128.9 (*C*H Ar), 130.5 (*C*H Ar), 130.0 (*C* Ar), 131.2 (*C* Ar), 131.4 (*C* Ar), 133.6 (*C* Ar), 134.0 (*C* Ar), 134.8 (*C* Ar), 135.7 (*C* Ar) ppm. $C_{26}H_{26}Cl_2N_2Pd$ (543.82): calcd. C 57.42, H 4.82, N 5.15; found C 57.61, H 4.73, N 5.07.

[PdCl$_2${(*R*,*R*)-5}] (9): This complex was synthesized according to the same procedure reported for **7**; yield 79%. ^{1}H NMR (300 MHz, CD_3CN): δ = 0.85 (s, 3 H, C*H*$_3$), 1.00 (s, 3 H, C*H*$_3$), 1.26 (m, 1 H), 1.70 (m, 1 H), 1.75 (m, 1 H), 1.92 (s, 3 H, C*H*$_3$), 2.10–2.35 (m, 3 H), 2.52 (m, 1 H), 2.66 (s, 3 H, NC*H*$_3$), 2.95 (m, 1 H), 2.97 (s, 3 H, NC′*H*$_3$), 3.67 (dd, *J* = 12 and 3 Hz, 1 H), 4.26 (dt, *J* = 8 and 3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 13.9 (*C*H$_3$), 19.1 (*C*H$_3$), 19.9 (*C*H$_3$), 26.9 (*C*H$_2$), 31.2 (*C*H$_2$), 41.5 (*C*H$_2$), 43.3 (*C*H), 51.4, 52.0, 53.6, 57.0, 58.8, 67.7, 196.9 (*C*=N) ppm. $C_{14}H_{26}Cl_2N_2Pd$ (399.68): calcd. C 42.07, H 6.56, N 7.01; found C 42.15, H 6.60, N 6.97.

[PdCl$_2${(*R*,*R*,*R*)-6}] (10): This complex was synthesized according to the same procedure reported for **7**; yield 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76 (s, 3 H, C*H*$_3$), 0.99 (s, 3 H, C*H*$_3$), 1.02 (s, 3 H, C*H*$_3$), 1.19 (m, 1 H), 1.51 (m, 1 H), 1.66–1.80 (m, 2 H), 1.82–1.92 (m 1 H), 2.06 (m, 1 H), 2.27 (dd, *J* = 13 and 3 Hz, 1 H), 2.50 (dd, *J* = 14 and 3 Hz, 1 H), 2.70–2.78 (m, 1 H), 2.80 (s, 3 H, NC′*H*$_3$), 3.02–3.09 (m, 2 H), 3.12 (s, 3 H, NC*H*$_3$), 4.19 (tt, *J* = 14 and 4 Hz, 1 H), 5.42 (b, 1 H, N*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4 (*C*H$_3$), 20.7 (*C*H$_3$), 20.8 (*C*H$_3$), 27.2 (*C*H$_2$), 38.3 (*C*H$_2$), 39.3 (*C*H$_2$), 45.0 (*C*H), 47.5 (*C*), 50.6 (*C*H$_2$N), 51.8 (*C*H$_3$N), 53.0 (*C*′H$_2$N), 53.9 (*C*′H$_2$N), 63.7 (*C*), 67.5 (*C*HN) ppm. $C_{14}H_{28}Cl_2N_2Pd$ (401.71): calcd. C 41.86, H 7.03, N 6.97; found C 42.03, H 6.91, N 6.92.

[Pd(R_a,*R*,*R*,*R*)-3][(η^3-PhCHCHCHPh)]OTf (11): To a yellow suspension of [Pd(η^3-PhCHCHCHPH)Cl]$_2$ (10 mg, 0.015 mmol) in acetone (5 mL), AgOTf (7.7 mg, 0.030 mmol) was added and consequently the solution became brightened in colour. After 1 h of stirring, the mixture was filtered through celite. The solvated species was left to react with a solution of the ligand (R_a,*R*,*R*,*R*)-**3** (14.2 mg, 0.06 mmol) in acetone (2 mL), and after 1 h the solvent was removed under reduced pressure. The brownish residue was dissolved in a small amount of dichloromethane and the complex was precipitated by slowly adding pentane while stirring. The resulting yellow solid was washed with three portions of pentane and dried under vacuum; yield 22 mg (80%). ^{1}H NMR (500 MHz, CD_2Cl_2), major isomer: δ = –0.03 (s, 3 H, C*H*$_3$), 0.65 (s, 3 H, C*H*$_3$), 0.98 (s, 3 H, C*H*$_3$), 1.06 (m, 1 H), 1.14 (m, 1 H), 1.48 (m, 1 H), 1.59 (m, 1 H, C*H*), 1.84 (m, 1 H), 1.97 (m, 1 H), 2.55–2.67 (m, 2 H), 2.80–2.96 (m, 2 H), 3.08 and 2.26 (AB, *J* = 13 Hz, 2 H, C*H*$_2$CH$_2$NH-), 3.41–3.55 (m, 2 H), 3.69 (m, 1 H), 4.22 and 2.93 (AB, *J* = 12 Hz, 2 H, ArC*H*$_2$N), 4.39 (d, *J* = 12 Hz, 1 H, *H*$_{anti}$), 4.56 (d, *J* = 12 Hz, 1 H, *H*′$_{anti}$), 6.26 (t, *J* = 12 Hz, 1 H, *H*$_{central}$), 6.78 (t, *J* = 7 Hz, 1 H), 7.22–7.50 (m, 10 H), 7.67 (m, 1 H), 7.81 (m, 2 H), 7.92 (m, 2 H), 7.97 (d, *J* = 8 Hz, 1 H), 8.19 (d, *J* = 8 Hz, 1 H), 8.28 (d, *J* = 8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (*C*H$_3$), 18.5 (*C*H$_3$), 20.5 (*C*H$_3$), 26.9 (*C*H$_2$), 38.2 (*C*H$_2$), 41.0 (*C*H$_2$), 45.0 (*C*H), 47.0 (*C*), 50.1 (*C*H$_2$), 50.6 (*C*), 58.9 (*C*H$_2$), 59.2 (Ar*C*H$_2$N), 59.7 (Ar*C*′H$_2$N), 73.1 (*C*HNH), 77.0 (*C*H$_{terminal}$), 79.7 (*C*H$_{terminal}$), 109.2 (*C*H$_{central}$), 126.5 (*C*H Ar), 126.6 (*C*H Ar), 126.9 (*C*H Ar), 127.1 (*C*H Ar), 127.4 (*C*H Ar), 128.2 (*C*H Ar), 128.3 (*C*H Ar), 128.7 (*C*H Ar), 128.8 (*C*H Ar), 129.1 (*C*H Ar), 129.2 (*C*H Ar), 129.6 (*C*H Ar), 130.8 (*C* Ar), 131.3 (*C* Ar), 132.3 (*C* Ar), 132.5 (*C* Ar), 133.9 (*C* Ar), 134.5 (*C* Ar), 134.8 (*C* Ar), 135.6 (*C* Ar), 137.2 (*C* Ar), 139.2 (*C* Ar) ppm. $C_{50}H_{50}F_3N_2O_3PdS$ (922.41): calcd. C 65.10, H 5.46, N 3.04; found C 65.32, H 5.20, N 3.08.

[Pd{(S_a)-4}(η^3-PhCHCHCHPh)]OTf (12): This complex was synthesized according to the same procedure reported for **11**; yield 92%. ^{1}H NMR (300 MHz, $CDCl_3$), major isomer: δ = 2.08 (s, 3 H, NC*H*$_3$), 2.27 (m, 1 H), 2.44 (d, *J* = 14 Hz, 1 H, ArC*H*$_2$N), 2.47 [m, 1 H, C*H*$_2$N(CH$_3$)$_2$], 2.51 (s, 3 H, NC′*H*$_3$), 2.82 (d, *J* = 12 Hz, 1 H, NC*H*$_2$CH$_2$N), 3.03 (m, 1 H, ArC′*H*$_2$N), 3.21 (d, *J* = 14 Hz, 1 H, ArC*H*$_2$N), 3.25 (m, 1 H, C*H*$_2$NMe$_2$), 4.44 (d, *J* = 12 Hz, 1 H, H$_{anti}$), 4.85 (d, *J* = 12 Hz, 1 H, ArC′*H*$_2$N), 5.12 (d, *J* = 11.9 Hz, 1 H, H$_{anti}$), 6.34 (t, *J* = 12 Hz, 1 H, H$_{central}$), 6.70 (dt, *J* = 8 and 1 Hz, 1 H), 7.25–7.15 (m, 3 H), 7.47–7.27 (m, 10 H), 7.61 (dt, *J* = 8 and 1 Hz, 1 H), 7.75 (m, 2 H), 7.85 (m, 2 H), 8.12 (d, *J* = 8 Hz, 1 H), 8.28 (d, *J* = 8 Hz, 2 H), 8.32 (d, *J* = 8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.0 (N*C*′H$_3$), 51.3 (N*C*H$_3$), 58.6 (N$_{az}$*C*H$_2$), 59.2 (N$_{az}$*C*′H$_2$), 59.9 (Me$_2$NCH$_2$*C*H$_2$), 60.0 (Me$_2$N*C*H$_2$CH$_2$), 75.4 (*C*$_{terminal}$), 78.9 (*C*′$_{terminal}$), 107.5 (*C*$_{central}$), 129.7–126.1 (*CH* Ar), 130.0 (*C* Ar), 130.9 (*C* Ar), 131.0 (*C* Ar), 132.0 (*C* Ar), 133.4 (*C* Ar), 134.0 (*C* Ar), 134.7 (*C* Ar), 135.9 (*C* Ar), 136.4 (*C* Ar), 136.7 (*C* Ar) ppm.

General Procedure for Palladium-Catalyzed Allylic Alkylations: In a 30 mL Schlenk tube equipped with a magnetic stirring bar, [Pd(η^3-C$_3$H$_5$)Cl]$_2$ (2.34 mg, 0.0064 mmol) was treated with the *N*,*N*-ligand (0.0130 mmol) in CH_2Cl_2 (0.7 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 30 min. After this time period, to the solutions 1-acetoxy-1,3-diphenylpropene (323 mg, 1.28 mmol), dimethyl malonate (338.2 mg, 2.56 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (520.8 mg, 2.56 mmol), and KOAc (6 mg, 0.06 mmol) were added sequentially, and the mixtures degassed. The reactions were monitored by TLC (hexane:AcOEt, 3:1), and after completion the mixtures were diluted with Et_2O and extracted with two portions of ice-cold saturated aqueous NH_4Cl solutions. The solutions were then dried ($MgSO_4$) and evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel, hexane:AcOEt, 5:1) to afford the products as a colourless oils. The enantiomeric excess values were determined by chiral HPLC (Chiralcel OD-H column) and the assignment of the absolute configurations was made by comparison with reported data.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra of dinitrogen ligands **1**–**6** and palladium complexes **6**–**12** are reported.

Acknowledgments

This work was supported by Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR), PRIN 2007HMTJWP_005.

[1] a) I. Ojima (Ed.), in: *Catalytic Asymmetric Synthesis*, 2nd ed., Wiley-VCH, New York, **2000**; b) G.-Q. Lin, Y.-M. Li, A. S. C. Chan (Eds.), in: *Principles and Applications of Asymmetric Synthesis*, Wiley-VCH, Weinheim, Germany, **2001**.

[2] a) B. M. Trost, D. L. van Vranken, *Chem. Rev.* **1996**, *96*, 395–422; b) B. M. Trost, T. Zhang, J. D. Sieber, *Chem. Sci.* **2010**, *1*, 427–440.

[3] T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691–1692.

[4] D. A. Lange, B. Goldfuss, *Beilstein J. Org. Chem.* **2007**, *3*, No. 36.

[5] G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **1993**, *26*, 339–345, and literature cited therein.

[6] For selected examples of the application of *P,P*-ligands in allylic substitution reactions, see: a) A. Saitoh, M. Misawa, T. Morimoto, *Tetrahedron: Asymmetry* **1999**, *10*, 1025–1028; b) E. Raluy, M. Diéguez, O. Pàmies, *J. Org. Chem.* **2007**, *72*, 2842–2850; c) J. Wassenaar, S. van Zutphen, G. Mora, P. Le Floch, M. A. Siegler, A. L. Spek, J. N. H. Reek, *Organometallics* **2009**, *28*, 2724–2734; d) F. Fernández, A. Gual, C. Claver, S. Castillón, G. Muller, M. Gómez, *Eur. J. Inorg. Chem.* **2010**, 758–766.

[7] a) A. Pfaltz, *Acc. Chem. Res.* **1993**, *26*, 339–345; b) H. Kubota, M. Nakajima, K. Koga, *Tetrahedron Lett.* **1993**, *34*, 8135–8138; c) P. G. Andersson, A. Harden, D. Tanner, P.-O. Norrby, *Chem. Eur. J.* **1995**, *1*, 12–16; d) P. Gamez, B. Dunjic, F. Fache, M. Lemaire, *Tetrahedron: Asymmetry* **1995**, *6*, 1109–1116; e) G. Chelucci, G. A. Pinna, A. Saba, *Tetrahedron: Asymmetry* **1998**, *9*, 531–534; f) J.-L. Vasse, R. Stranne, R. Zalubovskis, C. Gayet, C. Moberg, *J. Org. Chem.* **2003**, *68*, 3258–3270.

[8] D. Drommi, M. Saporita, G. Bruno, F. Faraone, P. Scafato, C. Rosini, *Dalton Trans.* **2007**, 1509–1519.

[9] M. Saporita, G. Bottari, G. Bruno, D. Drommi, F. Faraone, *J. Mol. Catal. A* **2009**, *309*, 159–165.

[10] For catalytic applications of camphor-based ligands, see: a) W. Oppolzer, *Pure Appl. Chem.* **1990**, *62*, 1241–1250; b) M. Knollmüller, M. Ferencic, P. Gärtner, K. Mereiter, C. R. Noe, *Tetrahedron: Asymmetry* **1998**, *9*, 4009–4020; c) A. Caselli, G. B. Giovenzana, G. Palmisano, M. Sistic, T. Pilati, *Tetrahedron: Asymmetry* **2003**, *14*, 1451–1454; d) A. Gayet, C. Bolea, P. G. Andersson, *Org. Biomol. Chem.* **2004**, *2*, 1887–1893; e) G. Chelucci, *Chem. Soc. Rev.* **2006**, *35*, 1230–1243; f) G. Blay, L. R. Domingo, V. Hernández-Olmos, J. R. Pedro, *Chem. Eur. J.* **2008**, *14*, 4725–4730.

[11] T. Mecca, S. Superchi, E. Giorgio, C. Rosini, *Tetrahedron: Asymmetry* **2001**, *12*, 1225–1233.

[12] J.-P. Mazaleyratt, D. J. Cram, *J. Am. Chem. Soc.* **1981**, *103*, 4585–4586.

[13] C. Rosini, R. Tanturli, P. Pertici, P. Salvadori, *Tetrahedron: Asymmetry* **1996**, *7*, 2971–2982.

[14] M. Widhalm, U. Nettekoven, H. Kalchhauser, K. Mereiter, M. J. Calhorda, V. Félix, *Organometallics* **2002**, *21*, 315–325.

[15] M. Diéguez, O. Pamies, *Acc. Chem. Res.* **2010**, *43*, 312–322.

Received: February 2, 2011
Published Online: May 10, 2011

