Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 18 (2007) 1742–1749

Quinolinophane-derived alkyldiphenylphosphines: two homologous P,N-planar chiral ligands for palladium-catalysed allylic alkylation

Renzo Ruzziconi,[a,*] Claudio Santi[b] and Sara Spizzichino[a]

[a] *Dipartimento di Chimica Università di Perugia, via Elce di Sotto, 8, 06123 Perugia, Italy*
[b] *Dipartimento di Chimica e Tecnologia del Farmaco, via Elce di Sotto, 8, 06123 Perugia, Italy*

Received 2 July 2007; accepted 9 July 2007

Abstract—Two novel homologous [2]paracyclo[2](5,8)quinolinophane-derived P,N-bidentate planar chiral ligands have been synthesised and their effectiveness in asymmetric catalysis tested in palladium-catalysed allylic malonylation of 1,3-diphenylpropenyl acetate. The extent of asymmetric induction depends linearly on the ligand/metal molar ratio, indicating the involvement of P,P-type and chelate P,N-type π-allylpalladium complexes in equilibrium. The length of the chain that binds the diphenylphosphine group to the quinolinophane moiety, while appreciably affecting the P,N-complex stability, has little effect on the extent of asymmetric induction, which is due to the greater reactivity of the [PN]-*exo–syn–syn*– ($[PN]_{xss}$) with respect to the [PN]-*endo–syn–syn*– ($[PN]_{nss}$) π-allylpalladium complex.

1. Introduction

Enantioselective palladium-catalysed allylic alkylation is one of the most valuable tools for stereoselective carbon–carbon bond-forming reactions.[1] To this end, many types of chiral ligands have been employed, among which the P,N-bidentate ones have been the most pursued, as testified by the myriad of chelating ligands tested in different enantioselective allylic alkylation reactions during the last decade.[2] The main reason for the increased interest in this class of ligands is the electronic differentiation of the electrophilic sites in square planar P,N-chelate allylpalladium complexes.[3] This is due to the different abilities of nitrogen and phosphorus to act as donor centres, as attack occurs regioselectively at the allylic terminus opposite to the phosphorus atom, which leads to the enantioselective formation of the alkylated product.[4]

Chiral phosphine–oxazoline ligands, developed by Pfaltz,[5] Helmchen[2b,4b,6] and Williams[7] have been the basis for many variants, which have the common feature of a 4-substituted oxazoline ring as an asymmetric element bonded to an aryldiphenylphosphine moiety. Several P,N-bidentate planar chiral ligands have also been synthesised and tested in asymmetric allylic alkylation reactions. To date, most investigations dealing with this class of ligands have been focused on chiral ferrocene derivatives, in which planar chirality is almost always associated with central chirality by a 4-alkyl- or 4-aryl-substituted oxazoline ring bonded to the ferrocene nucleus and located near the diphenylphosphino group.[8]

In spite of the substantial rigidity of the [2.2]paracyclophane backbone and its marked stability towards oxidation and relatively high temperatures, compared to the metallocene-based ligands, [2.2]paracyclophane derivatives have only received attention as planar chiral ligands of transition-metal catalysts during the last decade.[9] Chiral P,P-, N,O-, N,P- and N,N-type [2.2]paracyclophane-based ligands have been used in different transition-metal-catalysed stereoselective processes such as hydrogenation of carbon–carbon double bonds,[10] regio- and enantioselective epoxidations,[11] allylic alkylations,[12] and diethylzinc additions to aliphatic and aromatic aldehydes,[13] as well as ketone hydrosilylation.[14] During our research in the field of planar chiral ligands, special attention has been given to chiral derivatives of [2]paracyclo[2](5,8)quinolinophane.[15] This planar chiral heterocyclic compound was first used by Vögtle and Pfaltz to prepare enantiomerically pure 2-(pyridin-2-yl)-[2]paracyclo[2](5,8)quinolinophane, a N,N-bidentate ligand which was used in both copper-catalysed asymmetric cyclopropanation and iridium-catalysed asymmetric transfer-hydrogenation reactions.[16] We were

* Corresponding author. E-mail: ruzzchor@unipg.it

0957-4166/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2007.07.005

attracted by this uncommon system, reasoning that, with respect to planar 4,5-disubstituted [2.2]paracyclophane-based bidentate ligands (Fig. 1a), the quinolinophane moiety would allow the metal reaction centre to be orientated towards the stereogenic ethylenic bridge (Fig. 1b), therefore, inducing a higher stereoselectivity.

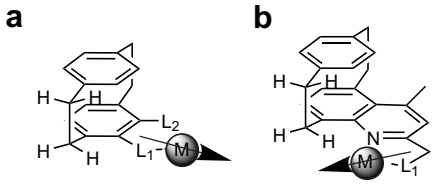
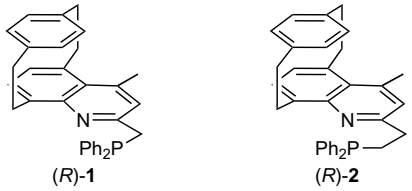


Figure 1.

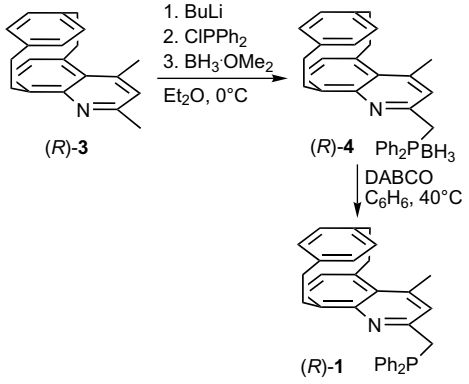
Accordingly, some enantiomerically pure (R_p)- and (S_p)-2-hydroxymethyl-4-methyl-[2]paracyclo[2](5,8)quinolinophanes were successfully used in the addition of diethylzinc to aromatic and aliphatic aldehydes to produce excellent standards of enantioselectivity.[17] These encouraging results prompted us to extend our investigation to planar chiral quinolinophanephosphine ligands in order to assess their effectiveness in stereoselective processes, as well as to investigate the effect that planar chirality has on the extent of asymmetric induction. Herein, we report the synthesis of two novel homologous planar chiral quinolinophanephosphine ligands (*R*)-**1** and (*R*)-**2** (Scheme 1), and its effectiveness in palladium-catalysed enantioselective allyllic alkylation reactions was also investigated.



Scheme 1.

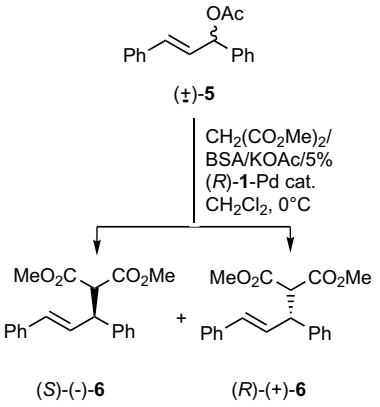
2. Results and discussion

The versatile (*R*)-(+)-2,4-dimethyl-[2]paracyclo[2](5,8)-quinolinophane **3**, which can be prepared on a multigram scale from enantiomerically pure (*R*)-(−)-4-amino[2.2]paracyclophane,[17b] is a suitable precursor for both ligands **1** and **2**. Deprotonation of **3** with butyllithium in diethyl ether, at 0 °C, involved the methyl group adjacent to the nitrogen, giving the 2-lithiomethylquinolinophane intermediate, exclusively.[17,18] The latter gave the (quinolinophan-2-yl)methyldiphenylphosphine borane complex (*R*)-**4** in 82% yield, at which point chlorodiphenylphosphine, and then the $BH_3{\cdot}OMe_2$ complex were added to the reaction mixture (Scheme 2). Finally, after the resulting air-stable borane complex (*R*)-**4** had been carefully purified by column chromatography, it was treated with DABCO, to obtain the expected quinolinophanephosphine (*R*)-**1** in 87% yield.



Scheme 2.

The ability of ligand (*R*)-**1** to induce stereoselectivity was tested in the classical palladium-catalysed alkylation of racemic 1,3-diphenyl-2-propenyl acetate **5** with dimethyl malonate anion, which gave a non-racemic mixture of methyl (*E*)-2-methoxycarbonyl-3,5-diphenylpent-4-enoate **6** (Scheme 3). The palladium complex catalyst (5 mol % with respect to substrate) was prepared by mixing the allylpalladium chloride dimer $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$[19] with 2 equiv of ligand (*R*)-**1** in dichloromethane (L/M = 1).



Scheme 3.

The nucleophilic species was generated in situ from dimethyl malonate and *N*,*O*-bis(trimethylsilyl)acetamide (BSA, 3 equiv) in the presence of a catalytic amount of potassium acetate, using the Trost procedure.[20] Under such conditions, there was 20% enantiomeric excess (ee) of the alkylated product in favour of the (*R*)-(+) enantiomer after 24 h, as determined by chromatographic analysis of the crude reaction mixture. The same result was obtained in two separate experiments in which the ligand/metal (L/M) molar ratio was increased to 1.5 and finally to 2.0. However, at L/M ratios less than 1.0, there was a linear drop in the ee values until at L/M = 0.5 and essentially a racemic mixture was obtained. If the L/M ratio decreased further, the ee increased linearly, but instead the enantiomer (*S*)-**6** was formed as the main alkylation product. Data are reported in Table 1 and plotted in Figure 2 (plot a).

A similar trend has already been observed by Burgess in an analogous study that made use of JM-Phos as ligand.[21] It

Table 1. Enantiomeric excess in the malonylation of 1,3-diphenyl-2-propenyl acetate catalysed by [(*R*)-**1**]–Pd complex

L/Pd[a]	Time (h)	Conversion[b] (%)	ee[c] (%)	Major enantiomer
—	3	0	—	—
2.0	3	100	20	(+)-(*R*)
1.5	3	100	20	(+)-(*R*)
1	3	100	20	(+)-(*R*)
0.5	3	100	3	(−)-(*S*)
0.25	3	90	12	(−)-(*S*)
0.13	3	10	25	(−)-(*S*)

[a] Pd, 0.01 equiv.
[b] 20 °C.
[c] Determined by HPLC analysis of the reaction mixture on a CHIRACEL-ODH column 0.46 × 25 cm, eluent, 98:2 hexane/isopropanol.

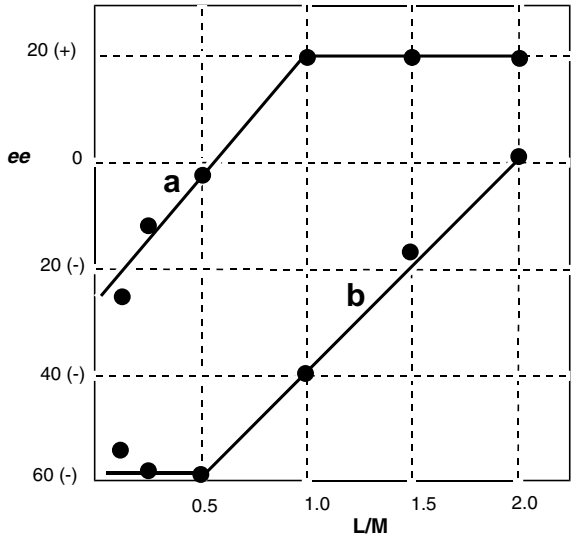
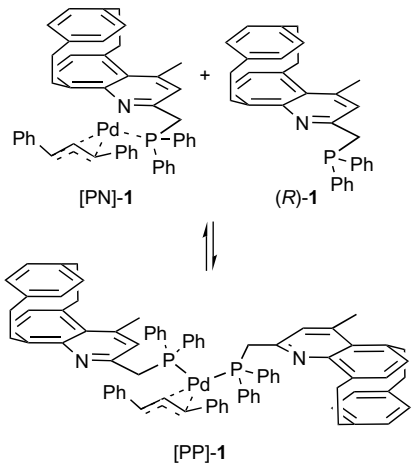


Figure 2. Ee value as a function of L/M molar ratio in the palladium-catalysed malonylation of 1,3-diphenylpropenyl acetate using (*R*)-**1** (plot a) and (*R*)-**2** (plot b) as a ligand.

seems to be a common trait of the P,N-type ligands having a diphenylphosphino group bonded by an alkyl chain to a stereogenic carbon adjacent to an sp^2 nitrogen. As suggested by Burgess, this trend can be explained by assuming that the reaction of the allylpalladium chloride dimer with 1,3-diphenylpropenyl acetate, in the presence of ligand (*R*)-**1**, generates two reactive species in equilibrium: a P,N-chelated allylpalladium complex [PN]-**1** and a P,P-type allylpalladium complex [PP]-**1** involving two molecules of the ligand (Scheme 4), the relative amounts of [PN]-**1** and [PP]-**1** depend on the stoichiometric L/M molar ratio.

Both complexes catalyse the allylic alkylation, even though the [PP]-**1** complex seems to be much more effective. In order to assess the composition of the mixture at different L/M ratios, we prepared a 0.0032 mM solution of the allylic complexes, by reacting diallylpalladium chloride dimer with 1 equiv of the ligand (*R*)-**1** (L/M = 0.5) in CD_2Cl_2, under an argon atmosphere.

After 1,3-diphenylpropenyl acetate was added, the ^{31}P NMR spectrum of the resulting mixture was quickly recorded. The spectrum showed three sharp singlets at δ 24.6, 22,8 and 18.2 ppm with a relative intensity of 1:1.2:0.14. In the first instance, the singlets at δ 24.6 and 22.8 were assigned to two [PN]-**1** complexes, while the singlet at δ 18.2 was attributed to the [PP]-**1** complex. Such an assignment was based on the observation that when more ligand (1.0 equiv) was added, the intensity of the singlet at δ 18.2 ppm was enhanced (relative intensity, 1:1.2: 0.5, respectively). On the basis of the ^{31}P NMR analysis reported by Reggelin and Helmchen for the palladium-catalysed allylic alkylation using phosphinoaryldihydrooxazole ligands,[4a] we provisionally ascribed the signal at δ 24.6 ppm to the *endo–syn–syn* $[PN]_{nss}$-**1** and the signal at 22.7 ppm to the diastereomeric *exo–syn–syn* $[PN]_{xss}$-**1** complex.[4b,22]



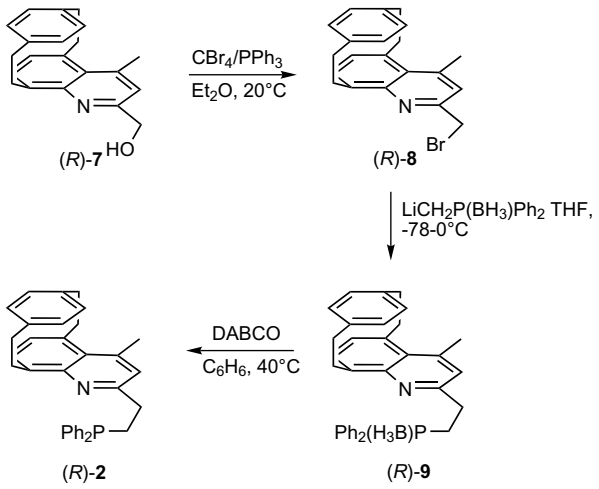
Scheme 4.

The fact that the ^{31}P signal of the presumed [PP]-**1** complex looks like a very sharp singlet, suggests that the two phosphorus atoms are equivalent and that nitrogen is not involved in the coordination to the metal. Clearly, the [PP]-**1** complex preferentially gives (*R*)-**6**, while the [PN]-**1** complex mixture gives the corresponding enantiomer (*S*)-**6** as the main alkylation product. Since the stoichiometric L/M ratio did not seem to have an effect on the *exo*/*endo* ratio, it substantially affected the [PN]/[PP] ratio, at first glance, the change of ee with the change in L/M ratio should depend on the [PN]/[PP] ratio. Unfortunately, due to the presence of the more reactive [PP]-**1** complex at any L/M ratio, the extent of asymmetric induction ascribed to [PN]-**1** cannot be assessed. However, if we consider the nucleophilic attack by malonate anion that occurs at the allylic carbon *anti* to the phosphorus atom, the preferential formation of the (*S*)-**6** enantiomer could be due to a greater reactivity of the exo–syn–syn– with respect to the diastereomeric *endo–syn–syn–*π-allyl complex. The slight preference for the formation of (*R*)-**6** from the nucleophilic attack over [PP] complex is more difficult to rationalise.

Since (*R*)-**6** can be formed by nucleophilic attack either at an *endo–syn–syn* ($[PN]_{nss}$-**1**) or at an *exo–anti–syn* ($[PN]_{xas}$-**1**) complex, the assignment of the ^{31}P NMR singlet at 24.6 to the former remain, at the moment, uncertain. Indeed, it has been reported that the intervention of the

exo–anti–syn allylic arrangement may become important in very overcrowded systems,[4c] as in this case.[23]

To get further, more reliable information about the structural features of the P,N-type complexes involved in the above process, we turned our attention to the homologous ligand which has a diphenylphosphino group bonded to the heterocyclic ring by an ethylenic bridge. We reasoned that a greater flexibility of the side-chain would have entailed a greater stability of the [PN] complexes, so as to allow a borderline L/M ratio to be determined, below which in the presence of [PP] complex in the reaction mixture can be excluded. This would allow a more complete investigation of the structural features of [PN] complexes. To this end, the available (*R*)-(−)-2-hydroxymethyl-4-methyl[2]paracyclo[2]-(5,8)quinolinophane **7**[17] was treated with CBr_4/PPh_3 in diethyl ether at room temperature and the corresponding bromomethyl derivative **8** was submitted to nucleophilic substitution by lithium (diphenylphoshine)methylide borane complex. The resulting 2-(quinolinophane)ethyldiphenylphosphine borane complex **9** was then treated with DABCO and the expected ligand (*R*)-**2** was recovered in 70% overall yield (Scheme 5).



Scheme 5.

Similar to ligand (*R*)-**1**, (*R*)-**2** was tested in the same allylic malonylation process. The trend of the ee values as a function of L/M stoichiometric ratio is reported in Table 2 and plotted in Figure 2 (plot b).

A linear increase of the ee value in favour of the (*S*)-**6** enantiomer was observed when the L/M ratio decreased from 2 to 0.5. At an L/M value >2, a racemic mixture of alkylated product was obtained, whereas at L/M <0.5, a practically constant ee value of 56 ± 2% was recorded. This trend, which was very similar to that already observed with ligand (*R*)-**1**, led us to conclude that, in this case, two catalytic species in equilibrium are also operating in the 2.0–0.5 L/M range, namely, a P,N-type π-allylpalladium complex [PN]-**2** and a P,P-type π-allylpalladium complex [PP]-**2** which involves two ligand molecules. Within this range, both species undergo nucleophilic attack, with [PP]-**2** being by far the most active one.[24] Outside this range a single species is operating: [PP]-**2** is the only species working at L/M >2; while [PN]-**2** complexes are running at L/M <0.5. Of course, the asymmetric induction is affected by the side-chain flexibility, as well as the significant distance of the metal from the quinolinophane moiety.

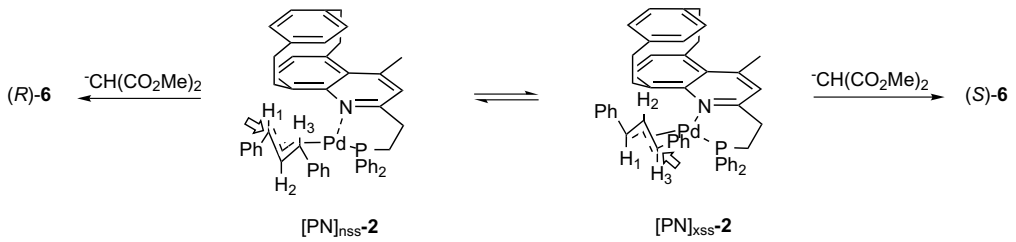
Table 2. Enantiomeric excess in the malonylation of 1,3-diphenyl-2-propen-1-yl acetate catalysed by [(*R*)-**2**]–Pd complex at variable L/M molar ratios

L/M ratio[a]	Time (h)	Conversion[b] (%)	ee[c] (%)	Configuration
2.0	24	100	2	(*R*)-(+)
1.5	24	100	17	(*S*)-(−)
1.0	24	100	39	(*S*)-(−)
0.5	24	60	58	(*S*)-(−)
0.25	24	25	57	(*S*)-(−)
0.125	24	10	54	(*S*)-(−)

[a] Pd, 0.01 equiv.
[b] 20 °C.
[c] Determined by HPLC analysis of the reaction mixture on a CHIRACEL-ODH column 0.46 × 25 cm, eluent, 98:2 hexane/isopropanol.

Thus, in the [PP]-**2**–Pd complex, the lengthening of the side-chain moves the metal further away from the asymmetric moiety than in the homologue [PP]-**1**–Pd complex; this would account for the drop in enantioselectivity at higher L/M ratios. Also in this case, the structural features of the [PN] ligands were investigated by preparing a 0.021 mM solution of the allylic complexes by reacting a diallyl palladium chloride dimer with 1.0 equiv of the ligand (*R*)-**2** (L/M = 0.5) in CD_2Cl_2, under an argon atmosphere. The ^{31}P NMR spectrum, registered immediately after the 1,3-diphenylpropenyl acetate was added, showed two singlets at δ 21.6 and 21.2 ppm with a relative intensity 1:1.3. Analogously to the ^{31}P NMR signals of the (*R*)-**1**-derived π-allylpalladium complexes, the two singlets were attributed to two [PN] bidentate complexes. As indicated by plot b of Figure 2, at L/M ratios <0.5, the P,P-type complex should be absent. This seems to be the case, as no peaks attributable to this kind of complex were found around 17.0 ppm. It is clear that at these L/M ratios, only the [PN]-type complex operates as a catalytic species. It is clearly seen that the major alkylated product (*S*)-**6** should be formed by the attack of the malonate anion at the carbon *anti* to the phosphorus atom of the most stable *exo–syn–syn* [PN]–π-allylpalladium complex ($[PN]_{xss}$-**2**), while the minor (*R*)-**6** enantiomer could be derived from an attack either at an *endo–syn–syn* ($[PN]_{nss}$-**2**) or at its diastereomer *exo–syn–anti* ($[PN]_{xas}$-**2**]) complex.

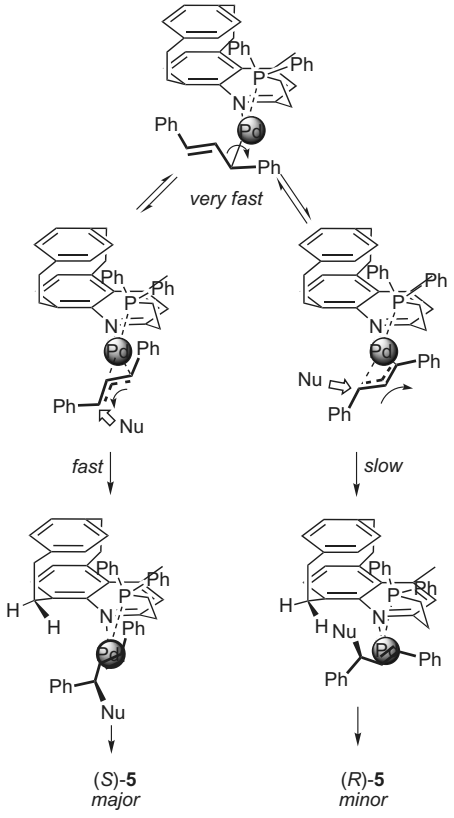
With the absence of [PP]-**2**, an NOE-based investigation on the structural features of the two [PN] complexes was now possible. The ^1H NMR spectrum of the complex mixture showed two sets of three signals each: the first one, with the signals located at δ 6.28 (dd, $J = 13.4$ and 11.1 Hz), 5.56 (d, $J = 13.4$ Hz) and 4.41 (d, $J = 11.1$ Hz) ppm was attributed to the allylic protons H-2, H-1 and H-3, respectively, of the major complex $[PN]_x$-**2** (Scheme 6). The signals of the second set located at δ 6.27 (dd, $J = 13.4$ and 10.3 Hz), 5.39 (d, $J = 13.4$ Hz) and 4.28 (d, $J = 10.3$ Hz), were attributed to the minor diastereomer $[PN]_n$-**2**. The coupling constants and, most importantly the absence of NOE effects between the allylic protons of each set, suggest



Scheme 6.

a *syn–syn* configuration for both the diastereomeric complexes (Scheme 6). Since they exhibit similar thermodynamic stabilities, ($[PN]_{xss}$-**2**/$[PN]_{nss}$-**2** = 1.3), the substantial ee value ($56 \pm 2\%$) obtained in the alkylation process has to be ascribed to kinetic rather than thermodynamic factors. Therefore, the $[PN]_{xss}$-**2** complex leading to the major product (*S*)-**6** should be about five times more reactive than the $[PN]_{nss}$-**2** one which gives the (*R*)-**6** enantiomer.

In this particular case, the different reactivity could be ascribed mostly to the substantial difference in the activation energy relative to the change from the η^3 to η^2 complex along the reaction path. Indeed, in the reaction of $[PN]_{xss}$-**2** with malonate, the counter-clockwise rotation of the allylic moiety around the Pd-allyl axis brings on a remarkable steric relaxation, while in the reaction of $[PN]_{nss}$-**2**, the analogous transformation implies a clockwise rotation of the allylic system, which would cause a substantial increase in the steric interactions (Scheme 7).



Scheme 7.

Such a hypothesis was substantiated by Helmchen in thorough structural and theoretical studies of palladium-catalysed allylic alkylation using chiral oxazolinephosphines as the ligand.[25]

After another 3.0 equiv of ligand was added (L/M = 2), the ^{31}P NMR spectrum was recorded again. Besides the peaks at δ 21.6 and 21.2 ppm, a new very sharp singlet appeared at δ 16.6 ppm, the relative intensity being 1.2:1.5:1, respectively. Analogous to the ^{31}P NMR spectrum of the complex mixture obtained with ligand (*R*)-**1**, the peak at 16.6 ppm was attributed to the [PP]-**2** complex. Interestingly, the $[PN]_{xss}$-**2**/$[PN]_{nss}$-**2** molar ratio ($\sim$1.3) remained unchanged; this indicates that a fast equilibrium takes place between the nearly isoenergetic *exo* and *endo* complexes. Again, [PP]-**2** complex is by far the most reactive species, thus, at this L/M stoichiometric ratio the reaction is very fast, and gives practically all racemic product.

3. Conclusion

In order to investigate the effects of planar chirality on the asymmetric palladium-catalysed enantioselective allylic alkylation, two homologous chiral P,N-bidentate ligands (*R*)-**1** and (*R*)-**2** were developed derived from (*R*)-2,4-dimethyl-[2]paracyclo[2](5,8)quinolinophane. Compound (*R*)-**1** differs from (*R*)-**2** only in the length of the carbon side-chain binding the diphenylphospine group to the quinolinophane moiety. Reactions of both ligands with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, in the presence of 1,3-diphenylpropenyl acetate, generate thermodynamic mixtures of *exo–syn–syn* and *endo–syn–syn* π-allylpalladium complexes ($[PN]_{xss}$ and $[PN]_{nss}$, respectively) and P,P-type π-allylpalladium complexes [PP], the latter involving two molecules of the ligand. The [PN]/[PP] ratio depends linearly on the stoichiometric ligand/metal molar ratio (L/M), while the $[PN]_x$/$[PN]_n$ molar ratio remains unchanged, indicating a fast equilibrium between these two species. The low $[PN]_{xss}$/$[PN]_{nss}$ ratio ($\sim$1.2–1.3) indicates that the two complexes are nearly isoenergetic. Due to the low stability of [PN]-**1** complexes, the most effective [PP]-**1** is present also at L/M $<$0.125. This make impossible to assess the actual ee value ascribable to [PN]-**1**. However, the value should not be dissimilar to that of [PN]-**2** complexes. If so, the structural difference between (*R*)-**1** and (*R*)-**2** has little or no influence on the relative reactivity of the corresponding [PN] complexes, nor on the mechanism of the allylic alkylation. The difference between the two ligands lies in a substantially higher stability of the [PN]-**2** with respect to the [PN]-**1** complexes. This is mainly due to the greater flexibil-

ity of the six-member heterocyclic ring, involving phosphorus, palladium and nitrogen, formed with (*R*)-**2**, compared with the homologous five member ring formed with (*R*)-**1**. This would allow the angle (θ) between the P–Pd–C-1 plane and that of the quinolinophane moiety to increase in [PN]-**2**, making the steric interactions less severe between the phenyl group at C-1 and the ethylenic bridge of quinolinophane (Fig. 3).

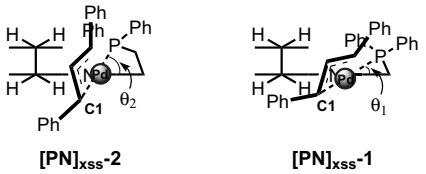


Figure 3.

4. Experimental

Unless specified, ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, in $CDCl_3$ solution using tetramethylsilane as an internal standard. ^{31}P NMR spectra were recorded at 162 MHz in $CDCl_3$ solution using 85% H_3PO_4 as an external standard. IR spectra were recorded in a FT-IR instrument in $CHCl_3$ solution in the 4000–400 cm^{-1} range. Optical activity was measured at 20 °C in $CHCl_3$ solution. The ee values were determined by HPLC analysis of the (1,3-diphenylallyl)malonate enantiomeric mixtures on a 0.46×25 cm Chiracel OD-H column.

4.1. Reagents and solvents

Chlorodiphenylphosphine and methyldiphenylphosphine borane complexes were prepared from commercial chlorodiphenylphosphine according to the procedures reported in the literature.[26] Racemic (*E*)-1,3-diphenylpropenyl acetate (±)-**5** was prepared by condensation of acetophenone with benzaldehyde, followed by the reduction of the resulting calcone with $NaBH_4$ in methanol and, finally, acetylation of the alcohol with acetic anhydride in CH_2Cl_2 in the presence of *N*,*N*-dimethylaminopyridine (DMAP) according to standard procedures. Bis-[(μ-chloro)(1,3-diphenylallyl)-palladium(II) was prepared following the procedure reported by Pregosin.[27] The starting material (*R*)-2,4-dimethyl[2]paracyclo[2](5,9)quinolinophane and (*R*)-2-hydroxymethyl-4-methyl[2]paracyclo[2](5,8)quinolinophane (*R*)-**7** were available from a previous work.[17] All the other commercial products were of the highest purity grade and used without further purification. Tetrahydrofuran and diethyl ether were distilled from KOH in the presence of CuCl and redistilled from sodium wires in the presence of benzophenone. CH_2Cl_2 was distilled from P_2O_5 after 2 h reflux.

4.2. (*R*)-2-[(Diphenylphosphino)methyl]-4-methyl[2]paracyclo[2](5,8)quinolinophane borane complex (*R*)-4

Butyllithium (1.63 M in hexanes, 1.1 mL, 1.74 mmol) was added to a solution of 2,4-dimethyl[2]paracyclo[2](5,8)-quinolinophane (0.5 g, 1.74 mmol) in diethyl ether (5 mL) at 0 °C under nitrogen. The cold bath was removed and the red–brown mixture was allowed to react for 2 h. After cooling at −75 °C, chlorodiphenylphosphine (0.31 mL, 0.38 g, 1.74 mmol) was added. A quick decolouration was observed after which, the mixture was allowed to react at 25 °C for 1 h. Borane dimethyl ether complex (1 M in THF, 1.74 mL, 1.74 mmol) was then added and the mixture was allowed to react under stirring for 1 h before it was poured into a mixture of ice and 5% aqueous HCl. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The collected organic phases were washed with water and dried over Na_2SO_4. After solvent evaporation, chromatography of the crude product on silica gel (eluent, 8:2 petroleum ether/CH_2Cl_2) allowed 0.51 g (63%) of a amorphous solid to be collected; mp 140–142 °C; $[\alpha]_D^{20} = +6.7$ (*c* 0.67, CH_2Cl_2); ^{1}H NMR δ 8.13–8.08 (m, 2H), 7.80–7.75 (m, 2H), 7.5 (m, 3H), 7.45–7.40 (m, 3H), 7.09 (s, 1H), 6.76–6.66 (four peaks, AB system, $J_{AB} = 7.2$ Hz, 2H), 6.43–6.36 (four doublets, split AB system, $J_{AB} = 7.9$ Hz, $^{4}J = 1.7$ Hz, 2H), 5.38 (dd, $J = 7.8$ and 1.7 Hz, 1H), 5.03 (d, $J = 7.8$ Hz, 1H), 4.15 (t, $J = 14$ Hz, 1H), 3.95 (dd, $J = 11$ and 3.4 Hz, 1H), 3.83–3.72 (eight peaks, AB portion of an ABX system, 2H), 3.10 (dd, $J = 13$ and 9.5 Hz, 1H), 2.93 (dt, $J = 14$ and 9.2 Hz, 1H), 2.81 (td, $J = 11$ and 3.4 Hz, 1H), 2.71 (td, $J = 12$ and 3.4 Hz, 1H), 2.64 (s, 3H), 2.56–2.46 (m, 2H); ^{13}C NMR δ 150.3 (d, $J =$ 3.7 Hz), 142.9, 139.3 139.1, 137.9, 136.9, 133.8, 133.3 (d, $J = 9.4$ Hz), 132.3, 132.1 (d, $J = 1.9$ Hz), 132.0, 131.5 (d, $J = 2.1$ Hz), 131.0 (d, $J = 2.1$ Hz), 130.8, 130.7, 130.3, 129.6, 128.9, 128.8 (d, $J = 1.6$ Hz), 128.7 (d, $J = 2.6$ Hz), 128.5, 127.9, 125.4 (d, $J = 2.7$ Hz), 38.0, 36.2 (d, $J =$ 32 Hz), 35.4, 34.3, 22.8; ^{31}P NMR δ 17.7 (m); IR ($CHCl_3$), ν_{max} 3021, 2928, 2855, 2388, 1589, 1437 cm^{-1}; Anal. Calcd for $C_{33}H_{33}BNP$: C, 81.65; H, 6.85; N,2.89. Found: C, 81.43; H, 6.70; N, 2.97.

4.3. (*R*)-2-[(Diphenylphosphino)methyl]-4-methyl[2]paracyclo[2](5,8)quinolinophane (*R*)-1

1,4-Diazabicyclo[2.2.2]octane (DABCO) (80 mg, 0.71 mmol) was added to a solution of (diphenylphosphino)methylquinolinophane borane complex (210 mg, 0.43 mmol) in degassed benzene (2 mL) under argon (*Caution*! Use of gloves under an efficient hood is prescribed) and the mixture was allowed to react at 50 °C for 3 h. The crude mixture was passed through a short column of argon-flowed silica gel (eluent, degassed 9:1 petroleum ether-diethyl ether mixture) in order to collect a white amorphous solid (180 mg, 82%): mp 68–70 °C; $[\alpha]_D^{20} =$ +3.1 (*c* 4.4, CH_2Cl_2); ^{1}H NMR δ 7.71 (td, $J = 7.5$ and 1.3 Hz, 2H), 7.59 (td, $J = 7.5$ and 1.3 Hz, 2H), 7.44–7.38 (Sym. m, 6H), 7.00 (s, 1H), 6.83–6.72 (four peaks, AB system, $J_{AB} = 7.2$ Hz, 2H), 6.45 (tight AB system, $J_{AB} =$ 7.1 Hz, 2H), 5.36–5.29 (four peaks, AB system, $J_{AB} =$ 7.7 Hz, 2H), 4.19 (br t, $J = 8.6$ Hz, 1H), 3.92 (d, $J = 13$ Hz, 1H), 3.83 (dd, $J = 14$ and 9.0 Hz, 1H), 3.73 (d, $J = 13$ Hz, 1H), 3.14 (dd, $J = 13$ and 9.5 Hz, 1H), 2.98 (dt, $J = 14$ and 9.1 Hz, 1H), 2.90–2.80 (m, 3H), 2.64 (s, 3H), 2.54 (dt, $J = 13$ and 9.0 Hz, 1H); ^{13}C NMR δ 155.2 (d, $J = 8.5$ Hz), 150.2, 143.0, 139.6, 139.3, 139.1,

138.4 (d, $J = 15$ Hz), 137.7, 136.7, 133.3, 133.1, 132.8 (d, $J = 19$ Hz), 132.3, 132.2 (d, $J = 10$ Hz), 130.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 123.7 (d, $J = 5.0$ Hz), 38.7 (d, $J = 15$ Hz), 37.8, 35.3, 34.3, 31.5; ^{31}P NMR δ −12.8 (s); IR ($CDCl_3$) ν_{max} 3016 (s), 2972, 2930, 2855, 1590 (s), 1506, 1435, 1380 cm^{-1}. Anal. Calcd for $C_{33}H_{30}NP$: C, 84.05; H, 6.41; N, 2.97. Found: C, 83.81; H, 6.29; N, 2.89.

4.4. (*R*)-2-(Bromomethyl)-4-methyl[2]paracyclo-[2](5,8)quinolinophane (*R*)-8

(Hydroxymethyl)quinolinophane (*R*)-**7** (1.0 g, 3.2 mmol) was dissolved in anhydrous diethyl ether (10 mL), after which CBr_4 (1.1 g, 3.2 mmol) and triphenylphosphine (0.86 g, 3.2 mmol) were added and the clear solution kept at 25 °C for 15 h. Fresh CBr_4 (0.54 g, 1.6 mmol) and triphenylphosphine (0.43 g, 1 6 mmol) were added and the mixture allowed to react for 3 h. The solvent was evaporated and the crude mixture filtered through a short column of silica gel eluting with a 9:1 petroleum ether/diethyl ether mixture. Flat white crystals were collected: mp, 158–160 °C; $[\alpha]_D^{20} = -11.5$ (*c* 0.5, $CHCl_3$); ^{1}H NMR δ 7.22 (s, 1H), 6.93–6.80 (four leaks, AB system, $J_{AB} = 7.2$ Hz, 2H), 6.48 (tight AB system, $J_{AB} = 8.4$ Hz, 2H), 5.87 (d, $J = 7.7$ Hz, 1H), 5.15 (d, $J = 7.7$ Hz, 1H), 4.74–4.66 (four peaks, AB system, $J_{AB} = 9.8$ Hz, 2H), 4.32 (br t, $J = 10$ Hz, 1H), 3.85 (dd, $J = 14$ and 9.1 Hz, 1H), 3.20–2.91 (m, 5H), 2.71 (s, 3H), 2.57 (dt, $J = 13$ and 9.0 Hz, 1H); ^{13}C NMR δ 152.7, 149.7, 144.2, 139.8, 139.6, 137.7, 137.0, 134.3, 132.7, 132.5, 131.2, 129.4, 128.6, 128.4, 122.8, 37.7, 35.2, 35.1, 34.5, 32.0, 22.7; IR ($CHCl_3$) ν_{max} 3016, 2972, 2930, 2855, 1590, 1506, 1435 cm^{-1}. Anal. Calcd for $C_{21}H_{20}BrN$: C, 68.86; H, 5.50; N, 3.82. Found: C, 68.70; H, 5.42; N, 3.89.

4.5. (*R*)-2-[2-(Diphenylphosphino)ethyl]-4-methyl[2]paracyclo[2](5,8)quinolinophane borane complex (*R*)-9

sec-Butyllithium (1.34 M in hexanes, 1.7 mL, 2.2 mmol) was added to a solution of methyldiphenylphosphine borane complex (0.46 g, 2.2 mmol) in anhydrous THF at −78 °C under an argon atmosphere while stirring. The mixture was allowed to react for 2 h before 2-(bromomethyl)-4-methyl[2]paracyclo[2](5,8)quinolinophane (0.80 g, 2.2 mmol) was added. The cold bath was removed and after the temperature had risen to 25 °C, the resulting yellow solution was poured into a mixture of ice and 5% aqueous HCl. The organic phase was separated and the aqueous phase extracted with diethyl ether (3 × 20 mL), and the collected organic phases were washed with water and dried over Na_2SO_4. After solvent evaporation, chromatography of the crude product on silica gel (eluent, 8:2 petroleum ether/diethyl ether) allowed 0.81 g (75%) of an amorphous white solid to be collected, which was identified as the phosphine borane complex: mp, 148–150 °C; $[\alpha]_D^{20} = +37$ (*c* 0.48, $CHCl_3$); ^{1}H NMR δ 7.85–7.76 (m, 4H), 7.52–7.44 (m, 6H), 6.91 (s, 1H), 6.89–6.76 (four peaks, AB system, $J_{AB} = 7.2$ Hz, 2H), 6.48 (br s, 2H), 5.67–5.44 (four peaks, AB system, $J_{AB} = 7.6$ Hz, 2H), 4.34 (br t, $J = 9.4$ Hz, 1H), 3.82 (dd, $J = 13$ and 9.4 Hz, 1H), 3.10–2.91 (m, 9H), 2.64 (s, 3H), 2.55 (dt, $J = 13$ and 9.0 Hz, 1H); ^{13}C NMR δ 156.9 (d, $J = 14$ Hz), 149.9, 143.4, 139.4, 139.2, 137.8, 137.0, 137.8, 137.0, 133.3, 132.5, 132.3, 132.2, (d, $J = 6.9$ Hz), 132.1, 131.2, 131.2 (d, $J = 2.1$ Hz), 129.9, 129.4 (d, $J = 20.9$ Hz), 129.0, 128.9, 128.9, 128.2, 127.7, 123.0, 37.6, 35.2, 34.6, 32.0, 31.3, 24.4 (d, $J = 37$ Hz), 22.6; ^{31}P NMR δ 16.0; IR ($CHCl_3$) ν_{max} 3023(vs), 2928, 2382(s), 1591, 1437, 1110, 1062 cm^{-1}. Anal. Calcd for $C_{34}H_{35}BNP$: C, 81.77; H, 7.06; N, 2.80. Found: C, 81.59; H, 7.12; N, 2.91.

4.6. (*R*)-2-[2-(Diphenylphosphino)ethyl]-4-methyl[2]paracyclo[2](5,8)quinolinophane (*R*)-2

The same procedure used to prepare (*R*)-**1** was used to prepare (*R*)-**2** starting from the quinolinophanephosphine borane complex (*R*)-**9** (0.20 g, 0.40 mmol). A white amorphous product was obtained and identified as quinolinophanephosphine (*R*)-**2** (0.18 g, 93%): mp 138–140 °C; $[\alpha]_D^{20} = +17$ (*c* 0.51, $CHCl_3$); ^{1}H NMR δ 7.5 (m, 4H), 7.4 (m, 6H), 6.91 (s, 1H), 6.88–6.74 (four peaks, AB system, $J_{AB} = 7.1$ Hz, 2H), 6.47 (br s, 2H), 5.78 (d, $J = 7.6$ Hz, 1H), 5.48 (d, $J = 7.6$ Hz, 1H), 4.33 (m, 1H), 3.83 (dd, $J = 14$ and 9.5 Hz, 1H), 3.15 (dd, $J = 12$ and 10 Hz, 1H), 3.08–2.89 (m, 6H), 2.71 (t, $J = 16$ Hz, 2H), 2.65 (s, 3H), 2.56 (dt, $J = 12$ and 9.3 Hz, 1H); ^{13}C NMR δ 158.6 (d, $J = 12$ Hz), 150.0, 143.1, 139.6, 139.3, 138.7, 138.8 (d, $J = 9$ Hz), 138.7 (d, $J = 19$ Hz), 137.8, 136.9, 133.1, 132.9 (d, $J = 18$ Hz), 132.8 (d, $J = 18$ Hz), 132.4, 132.2, 131.1, 128.7, 128.6 (d, $J = 7.0$ Hz), 128.4, 128.3, 128.0, 123.0, 37.6, 35.3, 34.6, 34.5 (d, $J = 21$ Hz), 32.0, 27.5 (d, $J = 12$ Hz), 22.7; ^{31}P NMR δ −15.56; IR ($CHCl_3$) ν_{max} 3018, 2928, 2855, 1591, 1436 cm^{-1}. Anal. Calcd for $C_{34}H_{32}NP$: C, 84.09; H, 6.64; N, 2.88. Found: C, 83.93; H, 6.72; N, 2.95.

4.7. General procedure for the palladium-catalysed allylic alkylation of 1,3-diphenyl-2-propen-1-yl acetate at variable L/M ratios

Six test tubes, fitted with a para rubber septum, filled with argon, after a few vacuum-argon cycles, were filled with variable volumes (from 30 to 80 μL) of the suitable ligand solution in degassed CH_2Cl_2 (5.0 mL, 5.17 M) followed by a degassed solution of diallylpalladium chloride dimmer (30 μL, 0.033 M). After stirring for 5 min, 0.5 mL of a freshly prepared solution of dimethyl malonate (0.75 g, 5.7 mmol), 1,3-diphenyl-2-propen-1-yl acetate (0.50 g, 2.0 mmol), potassium acetate (0.0016 g, 0.16 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (1.4 mL) in degassed CH_2Cl_2 (5 mL) was added and the mixture allowed to react at 20 °C for a suitable time. Water (1.0 mL) was added through the septum and, after 2 min of stirring, the organic phase was separated, dried over Na_2SO_4 and the solvent evaporated at reduced pressure. Preparative TLC on silica gel (eluent petroleum ether/diethyl ether 8:2) allowed enantiomeric mixtures of dimethyl (1,3-diphenyl-2-propen-1-yl)malonate to be isolated. The enantiomeric excesses were determined by HPLC analysis of the above mixtures on a CHIRACEL OD-H 0.46 × 25 cm column using a hexane/isopropanol 98:2 mixture as the eluent. Under such conditions, the retention times were 16.5 min and 17.7 min for (*R*)-(+)- and (*S*)-(−)-enantiomers, respectively.

Acknowledgements

Thanks are due to MUR (Ministero dell'Università e Ricerca) and the University of Perugia for financial support (PRIN 2004 Contract No. 2004033322). We also wish to express our sincere gratitude to Professor Thomas Rizzo dean of the Institute of Chemical Sciences and Engineering (ISIC) of the 'École Polytechnique Fédérale de Lausanne' (Epfl), for the donation of useful laboratory equipments.

References

1. (a) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2943; (b) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395–422; (c) Uenishi, J.; Hamada, M. *Tetrahedron: Asymmetry* **2001**, *12*, 2999–3006.
2. (a) Chelucci, G.; Orrù, G.; Pinna, G. A. *Tetrahedron* **2003**, *59*, 9471–9515; (b) Helmchen, G. *J. Organomet. Chem.* **1999**, *576*, 203–214; (c) Lautens, M. A.; Pfaltz, A. Allylic substitution reactions. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamanoto, H., Eds.; Springer: Heidelberg, 1999; Vol. 2, Chapter 24, (d) Jones, G.; Richards, C. J. *Tetrahedron: Asymmetry* **2004**, *15*, 653–664; (e) Bunlaksananusorn, T.; Luna, A. P.; Bonin, M.; Knochel, L.; Micouin, P. *Synlett* **2003**, 2240–2242; (f) Gilbertson, S. R.; Chang, C. W. T. *J. Org. Chem.* **1998**, *63*, 8424–8431.
3. (a) Cesarotti, E.; Demartin, F.; Grassi, M.; Prati, L. *J. Chem. Soc., Dalton Trans.* **1991**, 2073–2082; (b) Faller, J. W.; Chao, K.-H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231–1240.
4. (a) Steinhagen, H.; Reggelin, M.; Helmchen, G. *Angew. Chem., Int. Ed.* **1997**, *36*, 2108–2110; (b) Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelin, M.; Huttner, G.; Walter, O.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523–1526; (c) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031–1037.
5. (a) von Matt, P.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T.; Helmchen, G. *Tetrahedron: Asymmetry* **1994**, *5*, 573–584; (b) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566–567; (c) von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Ruegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265–284.
6. (a) Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769–1772; (b) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336–345.
7. Dawson, G. J.; Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 3149–3150.
8. (a) Zheng, W.-H.; Sun, N.; Hou, X.-L. *Org. Lett.* **2005**, *7*, 5151–5154; (b) Barbaro, P.; Bianchini, C.; Giambastiani, G.; Togni, A. *Tetrahedron Lett.* **2003**, *44*, 8279–8283; (c) Deng, W. P.; You, S.-L.; Hou, X.-L.; Dai, L.-X.; Xia, Y.-H.; Yu, W.; Sun, J. *J. Am. Chem. Soc.* **2001**, *123*, 6508–6519; (d) Zhang, W.; Yoneda, Y.-i.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron: Asymmetry* **1998**, *9*, 3371–3380; (e) Ahn, K. H.; Cho, C.-W.; Park, J.; Lee, S. *Tetrahedron: Asymmetry* **1997**, *8*, 1179–1185; (f) Bolm, C.; Hermanns, N.; Kesselgruber, M.; Hildebrand, J. P. *J. Organomet. Chem.* **2001**, *624*, 157–161.
9. Gibson, S. E.; Knight, J. D. *Org. Biomol. Chem.* **2003**, *1*, 1256–1269.
10. (a) Dominguez, B.; Zanotti-Gerosa, A.; Hems, W. *Org. Lett.* **2004**, *6*, 1927–1930; (b) Pye, P. J.; Rossen, K.; Reamer, R. A.; Tsou, N. N.; Volante, R. P.; Reider, P. *J. Am. Chem. Soc.* **1997**, *119*, 6207–6208; (c) Focken, T.; Raabe, G.; Bolm, C. *Tetrahedron: Asymmetry* **2004**, *15*, 1693–1706; (d) Bolm, C.; Focken, T.; Raabe, G. *Tetrahedron: Asymmetry* **2003**, *14*, 1733–1746.
11. Bolm, C.; Beckmann, O.; Kuhn, T.; Palazzi, C.; Adam, W.; Rao, P. B.; Saha-Moller, C. R. *Tetrahedron: Asymmetry* **2001**, *12*, 2441–2446.
12. (a) Whelligan, D. K.; Bolm, C. *J. Org. Chem.* **2006**, *71*, 4609–4618; (b) Wu, X. W.; Yuan, K.; Sun, W.; Zhang, M. J.; Hou, X. L. *Tetrahedron: Asymmetry* **2003**, *14*, 107–112; (c) Bolm, C.; Wenz, K.; Raabe, G. *J. Organomet. Chem.* **2002**, *662*, 23–33; (d) Wu, X. W.; Hou, X. L.; Dai, L. X.; Tao, J.; Cao, B. X.; Sun, J. *Tetrahedron: Asymmetry* **2001**, *12*, 529–532.
13. (a) Wu, X. W.; Zhang, T. Z.; Yuan, K.; Hou, X. L. *Tetrahedron: Asymmetry* **2004**, *15*, 2357–2365; (b) Danilova, T. I.; Rozenberg, V. I.; Starikova, Z. A.; Bräse, S. *Tetrahedron: Asymmetry* **2004**, *15*, 223–229; (c) Bräse, S.; Dahmen, S.; Höfener, S.; Lauterwasser, F.; Kreis, M.; Ziegert, R. E. *Synlett* **2004**, 2647–2669; (d) Danilova, T. I.; Rozenberg, V. I.; Sergeeva, E. V.; Starikova, Z. A.; Bräse, S. *Tetrahedron: Asymmetry* **2003**, *14*, 2013–2019.
14. Song, C.; Ma, C.; Ma, Y.; Feng, W.; Ma, S.; Chai, Q.; Andrus, M. B. *Tetrahedron Lett.* **2005**, *46*, 3241–3244.
15. Ricci, G.; Ruzziconi, R.; Giorgio, E. *J. Org. Chem.* **2005**, *70*, 1011–1018.
16. Worsdorfer, U.; Vögtle, F.; Glorius, F.; Pfaltz, A. *J. Prakt. Chem.* **1999**, *341*, 445–448.
17. (a) Ruzziconi, R.; Piermatti, O.; Ricci, G.; Vinci, D. *Synlett* **2002**, 747–750; (b) Ricci, G.; Ruzziconi, R. *Tetrahedron: Asymmetry* **2005**, *16*, 1817–1827.
18. Kaiser, E. M.; Bartling, G. J.; Thomas, W. E.; Nichols, S. B.; Nash, D. R. *J. Org. Chem.* **1973**, *38*, 71–75.
19. Togni, A. *Tetrahedron: Asymmetry* **1991**, *2*, 683–690.
20. Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143–1145.
21. Porte, A. M.; Reibenspies, J.; Burgess, K. *J. Am. Chem. Soc.* **1998**, *120*, 9180–9187.
22. The subscripts xss, xas and nss refer to diastereomeric π-allylpalladium complexes according to the meaning given by Faller and Helmchen: (a) Faller, J. W.; Chao, K. H. *J. Am. Chem. Soc.* **1983**, *105*, 3893–3898; (b) Kollmar, M.; Goldfuss, B.; Reggelin, M.; Rominger, F.; Helmchen, G. *Chem. Eur. J.* **2001**, *7*, 4913–4927.
23. Because of the overlapping of the ^{1}H and ^{13}C signals of the π-allylic system with those of the aromatic protons overlooking the quinoline moiety, ^{1}H and ^{13}C NMR spectra could not be used to sort out the structural features of the different palladium complexes present in the reaction mixture. Unfortunately, we were unable to obtain any crystals that were suitable for RX analysis.
24. By applying the pseudo-first order kinetic to the reaction of each π-allylpalladium complex with malonate anion, an approximate reactivity ratio $k_{[PP]}/k_{[PN]} > 120$ can be calculated from the data reported in Tables 1 and 2.
25. Kollmar, M.; Steinhagen, H.; Janssen, J. P.; Goldfuss, B.; Malinovskaya, S. A.; Vázquez, J.; Rominger, F.; Helmchen, G. *Chem. Eur. J.* **2002**, *8*, 3103–3114.
26. Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244–5252.
27. Barbaro, P.; Pregosin, P. S.; Salzmann, R.; Albinati, A.; Kunz, R. W. *Organometallics* **1995**, *14*, 5160–5170.