Allylpalladium(II) Complexes with Aminophosphane Ligands: Solution Behaviour and X-ray Structure ofcis-[Pd(η3-CH2CHCHPh)Ph2PCH2CHPhNH(2,6-C6H3iPr2)][PF6]

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Allylpalladium(II) Complexes with Aminophosphane ligands: Solution Behaviour and X-Ray Structure of *cis*-P [Pd(η^3-$CH_2CHCHPh$)($Ph_2PCH_2CHPhNH(2,6\text{-}C_6H_3(^iPr)_2)$,$PF_6$]

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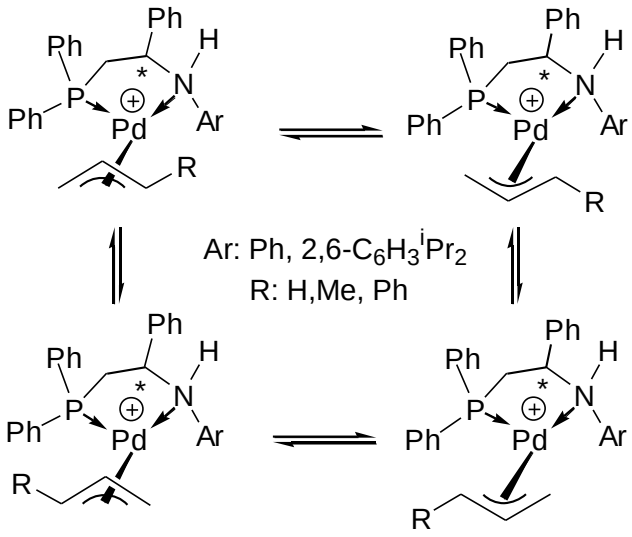
Abstract

A new β-aminophosphane, **L²** ($Ph_2PCH_2CH(Ph)NH(2,6\text{-}C_6H_3{}^iPr_2)$), bearing an asymmetric carbon atom and a vicinal prochiral nitrogen centre and (η^3-allyl)palladium complexes of general formula $[Pd(\eta^3\text{-}C_3H_4R)(\eta^2\text{-}Ph_2PCH_2CH(Ph)NHAr)]^+,[PF_6]^-$ (**1**-**6**) with R = H, Me or Ph and Ar = Ph or 2,6-$C_6H_3{}^iPr_2$, have been synthetised. NMR spectroscopic studies and a crystal structure analysis of complex **6** (R = Ph, Ar = 2,6-$C_6H_3{}^iPr_2$) confirmed the highly diastereoselective coordination of the nitrogen atom. Because of the allyl fluxionality and the presence of asymmetric centres, all the complexes exist in solution as mixtures of up to four diastereomers. For the monosubstituted allyl complexes $[Pd(\eta^3\text{-}C_3H_4R)(Ph_2PCH_2CH(Ph)NHAr)]^+,[PF_6]^-$ (R= Me or Ph) **3**-**6**, only *cis*/*trans*-P and *endo*/*exo* isomers with *syn*-oriented allyl substituents have been observed in solution. The diastereomeric distribution is subjected to a steric control since a modification of the steric bulk of the allyl substituents and/or N-aryl groups strongly affect the isomers ratio. An X-Ray diffraction study of compound **6** reveals a mixture of *endo* and *exo cis*-P *syn* isomers and corresponds to the first cis-P isomer crystal structure for a P,N-ligand allyl complex. A phase-sensitive 2-D NOESY NMR analysis shows that complex **1** undergoes a selective *syn*-*anti* exchange isomerisation, involving exclusively a *trans*-P opening of the η^3-allyl moiety. Therefore, η^3-η^1-η^3 rearrangements in allylic complexes **1**-**6** were assumed to occur *via* the regioselective formation of a σ-allyl intermediate.

Graphical abstract



Introduction

Palladium-catalyzed allylic substitution is a powerful methodology for the formation of new C-C or C-N bonds, with the potential to achieve high levels of enantioselectivity in the presence of chiral ligands.[1-4] In particular, the use of P-N ligands could allow very high enantioselectivities in the allylic alkylation of 1,3 diphenylpropenyl substrates.[5-10] One major advantage of hybrid ligands over bitopic ligands consists in the electronic differentiation of coordinative atoms, inducing a nucleophilicity discrimation of the terminal allylic carbon atoms. Therefore, other chiral hybrid ligands such as P-O,[11,12] P-S[13,14] or S-N[15,16] have been studied in order to benefit from the electronic parameter. The cationic allylic $[Pd(\eta^3\text{-allyl})L_2]^+$ complexes with bidendate L_2 ligands are defined as the key-intermediate in the catalytic cycle and there is a growing interest in understanding their dynamic behaviour in solution and in elucidating mechanistic details related to the enantiocontrol.[17-19] For complexes containing bitopic P,N ligands, the nucleophilic attack is assumed to occur at the carbon atom *trans* to phosphorus[17,27,28] and the selectivities strongly depend on the relative abundance of diastereomeric allylic complexes. In comparison to extensive investigations of complexes with symmetric allyl ligands, few studies have been devoted to monosubstituted allyl complexes.[17,20-26] In the case of the allylic alkylation of asymmetric substrates, such as cinnamyl acetate or crotyl acetate, only the trans-P diastereomers lead to the product containing the new chiral centre, whereas the cis-P isomers lead to an achiral linear Z or E products (see Figure 1). The enantiocontrol is therefore subordinate to the regiocontrol.

"Figure 1"

In a previous contribution, we have described the synthesis and the coordinative behaviour of a chiral aminophosphane, $Ph_2PCH_2CH(Ph)NHPh$ (**L^1**), in allyl palladium(II) complexes.[29] The study highlighted a diastereoselective N-coordination in the cationic complex $[Pd(\eta^3\text{-}C_3H_5)(L^1)]^+$, and a N-H•••Cl-M intramolecular interaction involving the dangling N-H moiety for the neutral complex $[PdCl(\eta^3\text{-}C_3H_5)(\kappa^1\text{:}P\text{-}L^1)]^+$ (see Figure 2) which is a feature of P-coordinated aminophosphanes with a secondary amine function.[30]

"Figure 2"

We report here the extension of our synthetic procedure to a new β-aminophosphane and to its cationic palladium allyl complexes, including ones with asymmetric monosubstituted allyl

ligands, as well as detailed 2-D NOESY NMR investigation of the mechanism of interconversion of the various diastereomers. The diastereomer ratio is strongly dependent on the steric bulk of the allyl N-substituents. The first X-Ray structure of a *cis*-P allyl complex is also presented.

Results and Discussion

Synthesis of the aminophosphane ligand L^2 and synthesis of cationic allyl palladium complexes

The new aminophosphane ligand $\mathbf{L^2}$ was synthetised by the same one-step procedure previously described for ligand $\mathbf{L^1}$ (Scheme 1).[29] It consists of the nucleophilic attack of an imine moiety by the diphenylphosphinomethyl anion. After hydrolysis and work-up, the aminophosphane was isolated in good yield as a light yellow microcrystalline powder and was characterized by ^{31}P, ^{13}C and ^{1}H NMR spectrometry and by elemental analysis (See Experimental Section). The ^{31}P NMR data are in agreement with those of other β-P,N ligands bearing an sp^3 nitrogen centre and an ethylenic backbone linking the heteroatoms.[29,31,32]

"Scheme 1"

The cationic allyl complexes **1**-**6** were synthetised by treatment of the chloro-bridged allylpalladium dimer with the appropriate ligand in the presence of an excess of the halide-scavenger $NaPF_6$ in dichloromethane. They were obtained in high yields as air-stable, white to yellow powders and are soluble in organic solvents except alkanes and Et_2O. The ^{31}P NMR chemical shifts for compounds **1**-**6** are characteristic for the aminophosphane bidentate coordination. Since the ligands contain an asymmetric centre, the complexes may exist as different diastereomers arising from the different face coordination (*endo* or *exo*) of the allyl moiety with respect to the ligand. The *endo* isomer was defined as having the C-H bond of the internal allylic carbon atom pointing in the same direction than the N-H bond (see Scheme 2). For the monosubstituted allyl complexes, the allyl substituents can be in a *cis*-P or *trans*-P position and can be positioned *syn* or *anti* with respect to the internal allyl proton. Furthermore, the nitrogen atom becomes a new asymmetric centre upon coordination. However, because of the induction by the vicinal chiral carbon atom, its coordination is expected to be highly diastereoselective, as previously reported.[29,33] Therefore, only 8 different diastereomers may arise in principle from the possible orientations of the allyl fragment. The diastereomeric distribution in solution at room temperature

was determined in each case by NMR spectroscopy (except for **1,** which has been already reported[29]) and is presented below.

NMR Studies on allylic compounds 1 and 2

The $^{31}P\{^{1}H\}$ NMR spectra of complexes **1** and **2** display 2 singlets in a 1:1 and 6.8:3.2 ratio, respectively. Because of the diastereoselective N-coordination and the allyl symmetry, compounds **1** and **2** may only afford two diastereomers (*endo* and *exo*, see Scheme 2). The diastereomeric ratio was confirmed by integration of the ^{1}H NMR spectra. The steric bulk of the N-substituents affects the isomeric proportion as observed for other allyl compounds (see below). This seems to be an important key for the enantiocontrol in allylic substitution of 1,3-propenylacetate derivatives.[8,18,19,34] For allylic complexes, the *endo/exo* ratio can be tuned by adjusting the steric constraints either around the donor atoms or on the allyl moiety.[14,19,35] You *et al.* have observed that, for a complex containing the 2-(Phenylthio)-1-(4-tertbutyloxazolinyl)ferrocene ligand an inversion of the configuration of the oxazoline ring asymmetric carbon slightly affects the *endo/exo* ratio (3.1:1 *versus* 2.1:1), whereas introducing two benzylic groups at the 4 position of the oxazoline ring strongly displaces the equilibrium in favour of the *endo* diastereomer.[36]

"Scheme 2"

The preferential nucleophilic attack at one specific allyl carbon atom is also one way to achieve high enantioselectivity. The difference between the ^{13}C chemical shifts of the external allyl carbon atoms ($\Delta\delta = \delta C_1 - \delta C_3$) is a measure of the difference between their electronic environment.[14,23,28,37] For complexes **1** and **2,** $\Delta\delta$ lies between 35.7 and 27.2 ppm depending on the isomer (See Table 1). Such a high $\Delta\delta$ is usual for P,N ligands, given the very different *trans* influence of the phosphorus and nitrogen atoms,[26] and reveals a higher electrophilicity for the C_1 atom (*trans*-P) than that for the C_3 atom (*cis*-P), see Scheme 2. This feature has also been observed in the solid state since Pd-C distances are longer for $C_{trans\text{P}}$ than those for $C_{cis\text{P}}$.[19,38-40] It is to be noted that the orientation of the allyl fragment induces slight differences for $\Delta\delta$ (35.7/32.5 for **1** and 29.9/27.2 for **2**).This feature probably arises from the steric hinderance caused by the N-substituents onto the allylic *trans*-P carbon atom, affecting its electrophilicity. Similar observations were made for allylic complexes with phosphinoxazoline ligands.[41] Therefore, there is a close relation between the N-substituents bulk and (*i*) the *endo*/*exo* ratio and (*ii*) the electrophilicity of the external carbon atoms.

"Table 1"

NMR characterization of monosubstituted allylic compounds 3-6

As detailed above, the introduction of one substituent on an external allyl carbon atom increases the number of possible isomers from two to eight. NMR investigations for complexes **3**-**6** revealed that all of them exist as mixtures of four diastereomers in solution in different equilibrium ratios. The coupling constants and chemical shifts for the allyl moieties are reported in Table 2. The $^{3}J(H,P)$, $^{2}J(C,P)$ and $\delta(^{13}C)$ are helpful for the assignment of each isomer as *trans*-P or *cis*-P, since the coupling constants to the phosphorus nucleus are greater for *trans* than for *cis* nuclei.[26,42] For the 1-butenyl complexes, the coupling constants involving the external methyl moiety, $^{4}J(H,P)$ and $^{3}J(C,P)$, enable the establishment of the *cis*-P/*trans*-P ratio, whereas the $\delta(^{1}H)$ is not diagnostic of the relative orientation. Indeed, for 1-butenyl (R= Me) complexes based on other types of P,N ligands, van Leeuwen proposed that the methyl $\delta(^{1}H)$ should be found at > 1.3 ppm when in the *trans*-P position and at < 0.6 ppm when in the *cis*-P position.[43] However, several ^{1}H resonances for the methyl substituents in complexes **3-6** and others described allylic complexes transgress this "rule".[19,20,44] For instance, the isomers of complexes **3** show resonances at 0.66, 1.04, 1.09 and 1.46 ppm (See Figure 3). In spite of this difficulty, the *cis*/*trans*-P orientation could be established unambiguously by others NMR characteristics.

"Table 2 and Figure 3"

The analysis of the $^{3}J(H_2,H_1)$ coupling constants allowed us to determine the relative positions of each allyl proton, revealing the exclusive presence of the *syn* isomers, *i.e.* having the protons H_1 and H_2 in *anti* position. This contrasts with 1,3 disubstituted allylic complexes, for which minor amounts of isomers with the allylic substituents in the *anti* position are present in solution.[28,45] The *syn*/*anti* ratio could be affected by tuning the steric bulk between the ligand substituents and the allyl moiety.[18,19,43] The four isomers and their proportion are depicted in Figure 4. Compounds **3** and **4** have been identified as 53:30:11:6 and 78:9:9:4 mixtures, respectively, with the two major isomers (**a** and **b**) having a *syn trans*-P orientation. The two minor isomers were assigned to the *syn cis*-P diastereomers (**c** and **d**). Concerning the *trans*-P isomers, it can be observed that the greater steric bulk introduced by the addition of the two isopropyl groups on the *ortho* positions of the N-phenyl substituent induces a strong variation of the *endo*/*exo* (or

exo/endo) ratio (from 53:30 for **3** to 78:9 for **4**), whereas the global *cis*/*trans*-P ratio is slightly affected (around 85:15). The geometry of the least abundant isomer of **4** (4% relative abundance) could not be unambiguously elucidated because of its very low concentration, coupled with the partial overlap of its resonances with those of the other isomers. Therefore, it was assumed to correspond to the second *cis*-P isomer of the **c**/**d** couple.

"Figure 4"

An influence of the steric bulk on the diastereomeric proportion is also present for the 1-phenylpropenyl complexes **5** and **6**, which were observed as 55:22:12:11 and 62:22:9:7 isomeric mixtures in solution, respectively. Contrary to the observations for compounds **3** and **4**, introducing a bulk N-substituent leads a strong variation of *cis*/*trans*-P ratio whereas the global *endo*/*exo* ratio is slightly affected. Nevertheless, the most remarkable observation is that the major isomer in solution is a *cis*-P isomer for complex **6**. Indeed, the major isomers for most[47] monosubtituted allyl complexes reported in the literature present a *trans*-P orientation.[17,20,23,43,44,46] To confirm this unexpected observation, suitable crystals were therefore grown and used for an X-Ray crystallographic study.

The solid state structure (discussed more in detail in a later section) highlights the *cis*-P orientation of the phenyl group and corresponds to a solid solution of both *endo* and *exo* isomers in a 78:22 ratio (see Figure 5). To the best of our knowledge, this represents the first solid state structural determination for an allylic P,N ligand in *cis*-P position. The crystals were redissolved in $CDCl_3$ and the resulting solution was monitored by ^{31}P NMR spectrometry (see

Figure 6). The spectrum displayed four singlets whose relative intensities evolved slowly from a 7:9:55:21 ratio (5 min) to the equilibrium 7:9:22:62 ratio after 24 hours. Therefore, the configuration of the two major isomers is completely established: the major isomer in solid state (*endo cis*-P, **6d**) displays the ^{31}P resonance at 29.68, whereas the major one in solution (^{31}P resonance at 21.85, **6c**) corresponds to the *exo cis*-P species.

"Figure 5 and

Figure 6"

As already shown for complexes **3** and **4**, the addition of the ^{i}Pr groups to the aryl *ortho* positions induced dramatic changes in the isomeric ratios on going from **5** and **6**, since it

approximately inverts the *trans*-P/*cis*-P ratio from 77/23 to 16/84. The free rotation around the C_{Ar}-N bond and the sterically demanding ^{i}Pr group destabilized the *trans*-P orientation of the allylic phenyl substituents. A similar behaviour was already observed by Helmchen and coworkers.[17,19,27] Therefore the subtle combination of steric repulsions between the allyl substituent and the N-group allowed a higher discrimation between the diastereomers. For the 1-butenyl complexes, **3** and **4**, the N-isopropyl groups favoured the *endo* isomer over the *exo* (or *vice-versa*) and destabilized the *cis*-P *versus* the *trans*-P isomers. The trend of tuning the *endo*/*exo* ratio has been reported mainly for symmetric disubstituted allyl complexes while few papers mentioned the *cis*/*trans* control.[17,23,43] All the complexes studied in this paper provided evidences of the influence of the steric bulkiness of the nitrogen substituent on the diastereomeric ratio.

Crystal structure of [Pd(η^3-$CH_2CHCHPh$)($Ph_2PCH_2CHPhNH(2,6\text{-}C_6H_3(^iPr)_2)$), PF_6], 6

Suitable yellow crystals of compound **6** grow from dichloromethane/pentane. As already mentioned above, the structure is quite interesting because it exhibits a solid solution of two different *cis*-P diastereomeric cations within the same unit cell. Indeed, due to disorder around the allyl carbon atoms accompanied by a slight tilting of the phenyl substituent, both *endo* and *exo cis*-P isomers have been identified in the solid state and their relative occupancies were refined to afford a 78/22 ratio in favour of the *endo* isomer (**6d**, see Figure 5). Such a cocrystallization phenomenom has many literature precedents for asymmetric allyl complexes[17,41,48-51] and allowed us to fully determine the major diastereomers not only in solid state but also in solution, as detailed in the previous section. An ORTEP view of the *endo* and *exo* diastereomers and selected crystallographic data are reported in Figure 5 and Table 4, respectively. Both isomers **6c** and **6d** exhibit a typical distorted square planar arrangement of the (η^3-allyl)Pd-P,N moiety.[17-19,28,41] The P-Pd-N bite angle of 84.89(6)° falls in the range observed for other compounds with five membered rings containing P,N ligands and the Pd-P (2.284(1) Å) and Pd-N (2.165(2) Å) bond lengths are similar to other reported values.[44,52-55] As a result of the different *trans* influence of the N and P atoms, the Pd-C(1) bond (2.187(4) Å) is longer than the Pd-C(3) bond (2.156(4) Å). The tilt angle α between the [C(1)-C(2)-C(3)] and [P-Pd-N] planes presented a value of 107.6°, which is in the wide range (100-120°) reported for other allylic compounds. The envelope conformation of the five membered chelate ring is characteristic for this kind of ligand in the solid-state.[29,33,56]

NMR-NOESY Studies of dynamic behaviour of complex 1

The fluxional behaviour of isomeric forms of $[Pd(\eta^3\text{-allyl})(L\text{-}L')]^+$ complexes in solution has been established as the consequence of different possible allyl isomerisation pathways or of the dissociation of the L-L' ligand.[4] The existence of a dynamic equilibrium between the two diastereomers of complex **1** in a 1:1 ratio has already been reported by us[29] and we then wished to clarify the allyl isomerisation pathway by recurring to 2-D NMR experiments. Therefore, a phase sensitive 2-D NOESY experiment in $CDCl_3$ solution was carried out. Similar experiments have previously been described for related compounds.[37,41,57] Figure 7 shows the results of this experiment and the most relevant exchange cross-peaks are labelled from *a* to *d*. The allyl ^1H resonances are labelled on the 1D spectrum for isomers **a** (*endo*) and **b** (*exo*) following the nomenclature of Scheme 2, the primed labels corresponding to the *exo* isomer.

"Figure 7"

The spectrum showed exchange cross-peaks for all the external allylic protons belonging to the *same* C atom, which revealed a η^3-η^1-η^3 isomerisation pathway. No exchange was observed between the H atoms on C_1 (*trans* to P) in **1a** and those on C_3 (*trans* to N) in **1b**, or *vice-versa*, thereby excluding an apparent allyl rotation. At the C_1 position, the H_{1s} proton in **1a** exchanged with the H'_{1s} proton in **1b**. Correspondingly, the H_{1a} proton in **1a** exchanged with the H'_{1a} proton in **1b**. Thus, each terminal allyl proton *trans* to P kept its relative position with respect to the internal allyl proton during the epimerization process. At the C_3 position, on the other hand, cross-peaks between the H_{3s} (and H_{3a}) proton in **1a** and H'_{3a} (and H'_{3s}) proton in **1b** were observed. Thus, only the two terminal allyl protons *trans* to N traded places in the process. These two latter observations are in agreement with a *syn-anti* exchange which implies the formation of a η^1-allyl intermediate by selective decoordination at the position *trans* to the phosphorus donor atom, followed by a C-C bond rotation and recoordination of the η^1-allyl double bond (See Scheme 3). This is consistent with the absence of any *anti cis*-P isomers for the monosubstituted complexes **3-6**. Other exchange cross-peaks were not observed. Notably, exchange peaks between H_{3s} and H'_{3s} and between H_{3a} and H'_{3a} were clearly absent. Because of the extensive overlap between the H_{1a} and H'_{1a} resonances, the absence of cross peaks between H_{1a} and H'_{1s} or between H_{1s} and H'_{1a} could not be unambiguously established, because any peak of this kind would be masked by the NOE peaks. However, we trust that we had sufficient evidence to conclude that a site-selective *syn-anti* exchange occurred at the C_3 atom.

"Scheme 3"

Therefore, we can conclude that a selective opening of the η^3-allyl *trans* to the phosphorus atom occurred and led exclusively to a *cis*-P σ-allyl intermediate during the η^3-η^1-η^3 isomerisation process. Such a selective process has already been described for chiral allyl complexes with P-based hybrid ligands resulting from the stronger *trans* influence of the P donor atom.[8,19,39,44] The only exception to this rule seems to involve a *cis*-P opening for a P,S ligand system.[14] For the other complexes reported here (**2**-**6**), we can assume a similar η^3-η^1-η^3 rearrangement *via* an exclusive *trans*-P opening. For the monosubstituted allyl compounds **3**-**6**, a second isomerisation pathway is necessary in order to interconvert the *cis*-P and *trans*-P isomers and this could involve an apparent allyl rotation. It seems likely that this pathway involves a Pd-C bond rotation after the selective *trans*-P opening (see Scheme 3). The same proposal was made by Krishnamurthy *et al*. to explain the *cis*/*trans* isomerisation of minor isomers in [Pd(η^3-1-PhC_3H_4)($Ph_2PN(^iPr)PPh${3,5-$N_2C_3HMe_2$})] complexes.[20]

Conclusion

The β-aminophosphane ligands, $Ph_2PCH_2CH(Ph)NHAr$ [Ar= Ph, (2,2-$C_6H_4{}^iPr_2$)] **L^1** and **L^2** bearing a prochiral nitrogen atom display a bidentate coordination mode in allylpalladium complexes. Because of the presence of an asymmetric centre vicinal to the weakly basic amine function, the metal coordination is highly diastereoselective. Different (η^3-allyl)palladium complexes of formula [Pd(η^3-1-C_3H_4R)L]$^+$,[PF_6]$^-$ (R = H, Me, Ph; L = **L^1**, **L^2**) have been synthesised and characterised in solution and in the solid-state. In solution, they display a dynamic behaviour between diastereomers because of a regioselective η^3-η^1-η^3 isomerization of the allyl moiety interconverting *endo*/*exo* (for **1**-**6**) and *cis*/*trans*-P (for **3**-**6**) isomers. Complexes **3**-**6** show exclusively the *syn* orientation of the allylic substituents and therefore give rise to a mixture of four diastereomers. The isomeric proportion depends on the steric bulk of the allylic and/or N-substituents. The dynamic behaviour of **1** was studied by 2-D NOESY experiments. These prove that the *syn*-*anti* exchange process occurs *via* a regioselective η^3-allyl opening *trans* to the phosphorus position. On the basis of these results, the exclusive formation of *cis*-P η^1-allyl intermediates was assumed to occur by an apparent allyl rotation which equilibrates the *cis* and *trans*-P isomers for the monosubstituted allyl complexes **3**-**6**. Work aimed at obtaining enantiomerically pure forms of these aminophosphane ligands is in progress permitting study of

palladium-catalyzed allylic alkylation of monosubstituted 1-propenyl substrates in order to correlate (or not) the regio-, stereo- and enantioselectivities with the observations described herein.

Experimental Section

All reactions were performed in Schlenk-type flasks under an argon atmosphere and solvents were purified and dried by conventional methods and distilled under argon. The ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker 300 Advance or a Bruker 500 DRX instrument. Complete assignment was achieved by use of COSY, DEPT and HMQC experiments. All chemical shifts are relative to $SiMe_4$ (^{1}H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR) and are given in ppm. Numbering scheme used for the **L²** ligand : H^a, H^b and H^c are the non-equivalent PCH_2 and the NCH protons, respectively. Numbering scheme used for the allyl ligand : C^1, C^2 and C^3 are *trans* to P atom, central carbon and *cis* to P atom respectively and H^s and H^a are *syn* and *anti* position relative to the internal proton H^2. For complexes **1** and **2**, the carbon and proton chemical shifts are noted C, H and C', H' respectively, for the endo and exo diastereomers (see Scheme 2). The elemental analyses were performed on a Fisons EA 1108 apparatus at the L.S.E.O. in Dijon. The reagents $^{n}BuLi$ (1.6 M in hexane), Ph_2PCH_3 and $NaPF_6$ were commercial products from Aldrich, and were used as received. N-benzylidene-2,6-diisopropylaniline[58] and the chloro-bridged allyl palladium dimers[59] $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, $[Pd(\eta^3\text{-}MeC_3H_4)(\mu\text{-}Cl)]_2$, $[Pd(\eta^3\text{-}PhC_3H_4)(\mu\text{-}Cl)]_2$ were prepared as previously described. The compound **1** and the ligand **L¹** have already been described in a previous publication.[29]

Synthesis of ligand L².

According to Peterson's method,[60] 5.0 mL of $^{n}BuLi$ (1.6 M in hexane, 8 mmol) was slowly added onto 1.2 mL of TMEDA (8 mmol) and the mixture was stirred at room temperature for 20 minutes. The methyldiphenylphosphine (1.5 mL, 8 mmol) was slowly added. The mixture was stirred further leading within 30 minutes to a bright yellow precipitate, which was dissolved by addition of few ml of THF. The solution was further stirred for half an hour and a solution of N-benzylidene-2,6-diisopropylaniline (1.65 g, 6.2 mmol) in 10 mL of THF was slowly added. The mixture was then stirred overnight, followed by hydrolysis with 20 mL of water. The water phase was separated and extracted three times with 20 mL of Et_2O. The combined organic phases were dried over $MgSO_4$ and the solvents were removed *in vacuo*. The product was recristallized from ethanol and yellowish needles were isolated by filtration and dried *in vacuo*. Yield: 1.59g (59%,). $C_{32}H_{36}NP$ (465.6): Calculated: C 82.55, H 7.79, N 3.01; found: C 82.25, H 8.05, N 3.48. ^{1}H NMR ($CDCl_3$, 300.13

MHz): δ= 0.89 (d, 6H, $^3J_{HH}$=6.5 Hz, CH-(C***H***$_3$)$_2$), 1.02 (d, 6H, $^3J_{HH}$=6.5 Hz, CH-(C***H***$_3$)$_2$), 2.77 (ddd, 1H, $^2J_{HP}$=1.0 Hz, $^3J_{HH}$=8.0 Hz, $^2J_{HH}$=13.5 Hz, PC***H*** ^{a}), 2.91 (ddd, 1H, $^2J_{HP}$=1.0 Hz, $^3J_{HH}$=8.0 Hz, $^2J_{HH}$=13.5 Hz, PC***H*** ^{b}), 3.00 (h, 2H, $^3J_{HH}$=6.7 Hz, C***H***-(CH$_3$)$_2$), 3.44 (broad s, 1H, exchange with D$_2$O, N***H***), 3.93 (dt, 1H, $^3J_{HH}$=$^3J_{HH}$=6.7 Hz, $^3J_{HP}$=8.2 Hz, NC***H***), 7.00 (m, 3H, ***H***$_{m,p}$ N-*Ph*), 7.14 (dd, 2H, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=7.9 Hz, ***H***$_m$ C-*Ph*), 7.25-7.35 (m, 15H, ***H***$_{arom}$). 7.40 (dt, 1H, $^4J_{HH}$=1.8 Hz, $^3J_{HH}$=7.0 Hz, ***H***$_o$ P-*Ph*), 7.45 (dt, 1H, $^4J_{HH}$=1.8 Hz, $^3J_{HH}$=7.0Hz, ***H***$_o$ P-*Ph*). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ= 24.3 (2C, 2 CH(***C***H$_3$)$_2$), 24.5 (2C, 2 CH(***C***H$_3$)$_2$), 28.2 (2C, 2 ***C***H(CH$_3$)$_2$), 36.1 (d, $^2J_{CP}$=14 Hz, P***C***H$_2$), 62.7 (d, $^3J_{CP}$=17 Hz, N***C***H), 123.7 (2C, 2 ***C***$_m$ N-*Ph*), 124.0 (***C***$_p$ N-*Ph*), 127.5 (2C, 2 ***C***$_m$ C-*Ph*), 127.9 (***C***$_p$ C-*Ph*), 128.75 (2C, 2 ***C***$_o$ C-*Ph*), 128.85 (2C, 2 ***C***$_m$ P-*Ph*)), 128.9 (2C, 2 ***C***$_m$ P-*Ph*), 129.0 (***C***$_p$ P-*Ph*), 129.2 (***C***$_p$ P-*Ph*), 132.9 (d, 2C, $^2J_{CP}$=19 Hz, 2 ***C***$_o$ P-*Ph*), 133.5 (d, 2C, $^2J_{CP}$=21 Hz, 2 ***C***$_o$ P-*Ph*), 138.9 (d, 1C, $^2J_{CP}$=12 Hz, 2 ***C***$_i$ P-*Ph*), 139.0 (d, 1C, $^2J_{CP}$=12 Hz, 2 ***C***$_i$ P-*Ph*), 141.1 (***C***$_i$ C-*Ph*), 143.0 (2C, ***C***$_o$ N-*Ph*), 143.1 (***C***$_i$ N-*Ph*). ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ= -23.2.

Synthesis of Palladium Complexes

[Pd(η^3-C$_3$H$_5$)(Ph$_2$PCH$_2$CHPhNH(2,6-C$_6$H$_3$(^{i}Pr)$_2$)), PF$_6$], (2)

To a solution of dimer [Pd(η^3-C$_3$H$_5$)Cl]$_2$ (97 mg, 0.26 mmol) in 5 mL of dichloromethane was progressively added a dichloromethane solution (5 mL) of ligand **L^2** (0.202 g, 0.53 mmol). The solution was stirred for 30 minutes at room temperature and transferred onto a suspension of NaPF$_6$ (0.223 g, 1.3 mmol) in 2 mL of dichloromethane. The mixture was further stirred for 2 hours and filtered through Celite. The yellow resulting filtrate was concentrated *in vacuo* to *ca*. 1 mL. Addition of 15 mL of pentane caused the precipitation of the product which was washed with pentane (2x20 mL). The white powder was filtered and dried under vacuum. Yield: 0.315 g (89%). C$_{35}$H$_{41}$F$_6$NP$_2$Pd (758.1): Calculated: C 55.45, H 5.45, N 1.84; found: C 55.34, H 5.70, N, 2.11. Major isomer (**2a,** 68%): ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ= 0.34 (d, 3H, $^3J_{HH}$=4.9 Hz, CH-(C**H**$_3$)$_2$), 0.62 (d, 3H, $^3J_{HH}$=4.9 Hz, CH-(C***H***$_3$)$_2$), 0.95 (d, 3H, $^3J_{HH}$=4.9 Hz, CH-(C***H***$_3$)$_2$), 1.15 (d, 3H, $^3J_{HH}$=4.9 Hz, CH-(C***H***$_3$)$_2$), 2.86 (m, 1H, C***H***-(CH$_3$)$_2$), 3.00 (dd, 1H, $^3J_{HP}$=3.7 Hz, $^3J_{HH}$=13.8 Hz, ***H*** ^{3a}), 3.14 (dt, 1H, $^3J_{HH}$=2.9 Hz, $^2J_{HP}$=$^2J_{HH}$=15.0 Hz, PC***H***), 3.24 (m, 1H, C***H***-(CH$_3$)$_2$), 3.66 (dt, 1H, $^3J_{HH}$=3.6 Hz, $^2J_{HP}$=$^2J_{HH}$=15.0 Hz, PC***H***), 3.84 (t, 1H, $^3J_{HP}$=$^3J_{H1sH2}$=5.9 Hz, ***H*** ^{1s}), 4.03(m, 1H, NC***H***), 4.16 (d, 1H, $^3J_{HH}$=6.8 Hz, ***H*** ^{3s}), 4.21 (dd, 1H, $^3J_{HP}$=8.9 Hz, $^3J_{HH}$=14.1 Hz, ***H*** ^{1a}), 5.51 (apparent tt, 1H, $^3J_{H2H1s}$=$^3J_{H2H3s}$=6.9 Hz, $^3J_{H2H1a}$=$^3J_{H2H3a}$=13.8 Hz, ***H*** ^{2}), 6.68 (d, 1H, $^3J_{HH}$=10.8 Hz, N***H***), 6.91-7.76 (m, merged with second diastereomer aromatic protons, ***H***$_{arom}$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$): δ= 23.9 (CH-(***C***H$_3$)$_2$), 24.2 (CH-(***C***H$_3$)$_2$), 24.5 (CH-(***C***H$_3$)$_2$), 24.8 (CH-(***C***H$_3$)$_2$), 28.3 (2 ***C***H-(CH$_3$)$_2$), 35.7 (d, $^2J_{CP}$=25 Hz, P***C***H$_2$), 52.4 (***C*** ^{3}), 66.9 (d, $^3J_{CP}$=7 Hz, N***C***H), 82.3 (d, $^2J_{CP}$=27 Hz, ***C*** ^{1}),

120.3 (d, $^2J_{CP}$=5 Hz, ***C*^{2}**), 124.6-140.4 (m, 24C, ***C***$_{arom}$). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ= 30.71 (s), -142.75 (hept, $^1J_{PF}$=716 Hz, PF_6^-). Minor isomer (**2b,** 32%): ^{1}H NMR : δ= 0.28 (d, 3H, $^3J_{HH}$=5.3 Hz, CH-(C***H***$_3$)$_2$), 0.69 (d, 3H, $^3J_{HH}$=5.3 Hz, CH-(C***H***$_3$)$_2$), 1.09 (d, 3H, $^3J_{HH}$=5.3 Hz, CH-(C***H***$_3$)$_2$), 1.13 (d, 3H, $^3J_{HH}$=5.3 Hz, CH-(C***H***$_3$)$_2$), 2.77 (m, 1H, C***H***-(CH$_3$)$_2$), 2.96-3.00 (m, 2H, ***H*^{1s}** and ***H*^{3a}**), 3.10 (dt, 1H, $^3J_{HH}$=3.0 Hz, $^2J_{HP}$=$^2J_{HH}$=14.8 Hz, PC***H***), 3.46 (dt, 1H, $^3J_{HH}$=4.0 Hz, $^2J_{HP}$=$^2J_{HH}$=14.8 Hz, PC***H***), 3.61 (m, 1H, H, C***H***-(CH$_3$)$_2$), 3.90 (d, 1H, $^3J_{HH}$=5.9 Hz, ***H*^{3s}**), 4.19 (m, NC***H***), 4.35 (dt, $^2J_{HH}$=2.1 Hz, $^3J_{HP}$=$^3J_{HH}$=8.1 Hz, ***H*^{1a}**), 6.02 (apparent tt, 1H, $^3J_{H2H1s}$=$^3J_{H2H3s}$=6.4 Hz, $^3J_{H2H1a}$=$^3J_{H2H3a}$=12.9 Hz, ***H*^{2}**), 6.47 (d, 1H, $^3J_{HH}$=9.8 Hz, N***H***), 6.88-7.76 (m, merged with major diastereomer aromatic proton, ***H***$_{arom}$). $^{13}C\{^1H\}$ NMR : δ= 23.4 (CH-(***C***H$_3$)$_2$), 23.7 (CH-(***C***H$_3$)$_2$), 24.2 (CH-(***C***H$_3$)$_2$), 24.4 (CH-(***C***H$_3$)$_2$), 28.2 (2 ***C***H-(CH$_3$)$_2$), 35.7 (d, $^2J_{CP}$=25 Hz, P***C***H$_2$), 53.4 (***C*^{3}**), 66.9 (d, $^3J_{CP}$=5 Hz, N***C***H), 80.6 (d, $^2J_{CP}$=29 Hz, ***C*^{1}**), 122.2 (d, $^3J_{CP}$=5 Hz, ***C*^{2}**), 124.4-139.8 (m, 24C, ***C***$_{arom}$). $^{31}P\{^1H\}$ NMR : δ= 29.61 (s).

The complexes (**3**-**6**) were synthetised by following the same procedures as described above for the preparation of complex **2**.

[Pd(η^3-CH$_2$CHCHMe)(Ph$_2$PCH$_2$CHPhNHPh),PF$_6$], (3)

Starting materials : [Pd(η^3-MeC$_3$H$_4$)Cl]$_2$ (54 mg, 0.14 mmol), **L^1** (104 mg, 0.27 mmol) and $NaPF_6$ (95 mg, 0.56 mmol). Yield: 0.164 g (88%). $C_{30}H_{31}F_6NP_2Pd$ (687.9): Calculated: C 52.37, H 4.54, N 2.04 ; found: C 52.23, H 4.89, N 2.34. Major *trans*-P isomer (**3a**, 53%): ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ= 0.66 (dd, 3H, $^3J_{HH}$=6.3 Hz, $^4J_{HP}$=9.3 Hz, C***H*$_3$**), 2.56 (dd, 1H, $^2J_{HH}$=2.1 Hz, 3J_{HH}=11.8 Hz, ***H*^{3a}**), 2.96 (dt, 2H, $^3J_{HH}$=2.9 Hz, $^2J_{HP}$=$^2J_{HH}$=14.6 Hz, PC***H*** et PC***H'***), 3.32 (dt, 1H, $^3J_{HH}$=2.6 Hz, $^2J_{HP}$=$^2J_{HH}$=14.3 Hz, PC***H***), 3.79 (dd, 1H, $^2J_{HH}$=2.6 Hz, $^3J_{HH}$=6.8 Hz, ***H*^{3s}**), 3.94 (m, 1H, NC***H***), 4.98 (m, 1H, ***H*^{1a}**), 5.23 (dt, 1H, $^3J_{HH}$=6.3 Hz, 3J_{HH}=3J_{HH}=14.6 Hz, ***H*^{2}**), 6.21 (d, 1H, $^3J_{HH}$=11.4 Hz, N***H***), 6.87-7.83 (m, merged with others diastereomers aromatic protons, ***H***$_{arom}$). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ= 14.1 (d, $^3J_{CP}$=4 Hz, ***C*^{4}**). 35.9 (d, $^2J_{CP}$=23 Hz, P***C***H$_2$), 46.7 (d, $^2J_{CP}$=4 Hz, ***C*^{3}**), 68.4 (d, $^3J_{CP}$=10 Hz, N***C***H), 102.9 (d, $^2J_{CP}$=26 Hz, ***C*^{1}**), 116.2 (d, $^2J_{CP}$=5 Hz, ***C*^{2}**), 121.4-144.1 (m, 24C, ***C***$_{arom}$). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ= 32.95 (s), -142.69 (hept, $^1J_{PF}$=716 Hz, PF_6^-). Minor *trans*-P isomer (**3b**, 30%): ^{1}H NMR: δ= 1.04 (dd, 3H, $^3J_{HH}$=6.3 Hz, $^4J_{HP}$=9.1 Hz, C***H*$_3$**), 2.82 (d, 1H, $^3J_{HH}$=10.1 Hz, ***H*^{3a}**), 3.18 (dt, 1H, $^3J_{HH}$=3.2 Hz, $^2J_{HP}$=$^2J_{HH}$=14.6 Hz, PC***H***), 3.54 (dd, 1H, $^2J_{HH}$=2.2 Hz, $^3J_{HH}$=6.8 Hz, ***H*^{3s}**), 3.92 (m, 1H, ***H*^{1a}**), 4.08 (m, 1H, NC***H***), 5.58 (dt, 1H, $^3J_{HH}$=6.9 Hz, ^3JH$_2$H$_{1a}$=$^3J_{HH}$=13.8 Hz, ***H*^{2}**), 5.87 (d, $^3J_{HH}$=11.3 Hz, N***H***), 6.96-7.91 (m, merged with others diastereomers aromatic protons, ***H***$_{arom}$). $^{13}C\{^1H\}$ NMR: δ= 14.2 (d, $^3J_{CP}$=4 Hz, ***C*^{4}**), 35.5 (d, $^2J_{CP}$=23 Hz, P***C***H$_2$), 47.5 (d, $^2J_{CP}$=3 Hz, ***C*^{3}**), 68.8 (d, $^3J_{CP}$=10 Hz, N***C***H), 101.7 (d, $^2J_{CP}$=26 Hz, ***C*^{1}**), 118.9

(d, $^2J_{CP}$=5 Hz, ***C*^{2}**), 144.4-121.5 (m, 24C, ***C***$_{arom}$). $^{31}P\{^1H\}$ NMR: δ= 32.05 (s). Isomer *cis*-P (**3c**, 11%). ^{1}H NMR: δ= 1.09 (dd, 3H, $^3J_{HH}$=6.3 Hz, $^4J_{HP}$=9.1 Hz, C***H***$_3$), 2.72 (broad d, $^3J_{HH}$=6.9 Hz, ***H*^{1s}**), 4.17 (m,1H, ***H*^{1a}**), 5.73 (m, 1H, ***H*^{2}**), 6.25 (d,1H, $^3J_{HH}$=11.1 Hz, N***H***). $^{13}C\{^1H\}$ NMR: δ= 17.2 (***C*^{4}**), 72.3 (d, $^2J_{CP}$=5 Hz, ***C*^{3}**), 78.3 (d, $^2J_{CP}$=23 Hz, ***C*^{1}**), 123.5 (d, $^2J_{CP}$=6 Hz, ***C*^{2}**). $^{31}P\{^1H\}$ NMR: δ= 32.10 (s). Isomer *cis*-P (**3d**, 6%): ^{1}H NMR: δ= 1.46 (dd, 3H, $^3J_{HH}$=6.3 Hz, $^4J_{HP}$=9.1 Hz, C***H***$_3$), 2.81 (m, 1H, ***H*^{1s}**), 5.68 (m, 1H, ***H*^{2}**), 6.40 (d,1H, $^3J_{HH}$=11.0 Hz, N***H***). $^{13}C\{^1H\}$ NMR: δ= 18.0 (***C*^{4}**), 69.2 (d, $^2J_{CP}$=4 Hz, ***C*^{3}**), 74.2 (d, $^2J_{CP}$=25 Hz, ***C*^{1}**). $^{31}P\{^1H\}$ NMR: δ= 28.63 (s).

[Pd(η^3-CH$_2$CHCHMe)(Ph$_2$PCH$_2$CHPhNH(2,6-C$_6$H$_3$(^{i}Pr)$_2$),PF$_6$], (4)

Starting materials : [Pd(η^3-MeC$_3$H$_4$)Cl]$_2$ (47 mg, 0.12 mmol), **L^2** (112 mg, 0.24 mmol) and NaPF$_6$ (48 mg, 0.29 mmol). Yield : 0.149 g (81%). C$_{36}$H$_{43}$F$_6$NP$_2$Pd (772.1): C 56.00, H 5.61, N 1.81; found: C 55.81, H 5.77, N 2.14%. Major *trans*-P isomer (**4a**, 78%): ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ= 0.36 (d, 3H, $^3J_{HH}$=6.6 Hz, CH-(C***H***$_3$)$_2$), 0.67 (dd, 3H, $^3J_{HH}$=6.6 Hz, $^4J_{HP}$=9.4 Hz, ***C*^{4}*H*$_3$**), 0.69 (d, 3H, $^3J_{HH}$=6.6 Hz, CH-(C**H**$_3$)$_2$), 1.03 (d, 3H, $^3J_{HH}$=6.6 Hz, CH-(C***H***$_3$)$_2$), 1.17 (d, 3H, $^3J_{HH}$=6.6 Hz, CH-(C***H***$_3$)$_2$), 2.68 (h, 1H, $^3J_{HH}$=6.6 Hz, C***H***-(CH$_3$)$_2$), 2.83 (dd, 1H, $^2J_{HH}$=1.9 Hz, $^3J_{HH}$=12.2 Hz, ***H*^{3a}**), 3.20 (h, 1H, $^3J_{HH}$=6.4 Hz, C***H***-(CH$_3$)$_2$), 3.27 (dt, 1H, $^3J_{HH}$=3.0 Hz, $^2J_{HP}$=$^2J_{HH}$=15.0 Hz, PC***H***), 3.55 (dt, 1H, $^3J_{HH}$=3.5 Hz, $^2J_{HP}$=$^2J_{HH}$=14.8 Hz, PC***H***), 4.10 (dd, 1H, $^2J_{HH}$=2.6 Hz, ^3JH$_{3s}$H$_2$=7.0 Hz, ***H*^{3s}**), 4.14 (m, 1H, NC***H***), 4.75 (m, 1H, ***H*^{1a}**), 5.34 (dt, 1H, $^3J_{H2H3s}$=7.0 Hz, $^3J_{H2H1a}$=$^3J_{H2H3a}$=12.4 Hz, ***H*^{2}**), 6.26 (d, 1H, $^3J_{HH}$=10.9 Hz, N***H***), 6.94-7.47 (m, merged with other diastereomers aromatic protons, ***H***$_{arom}$). $^{13}C\{^1H\}$ NMR (125.7 MHz, CDCl$_3$): δ= 15.7 (d, $^2J_{CP}$=4 Hz, ***C*^{4}**), 23.1 (CH-(***C***H$_3$)$_2$), 24.3 (CH-(***C***H$_3$)$_2$), 24.9 (CH-(***C***H$_3$)$_2$), 25.2 (CH-(***C***H$_3$)$_2$), 28.2 (***C***H-(CH$_3$)$_2$), 29.2 (***C***H-(CH$_3$)$_2$), 35.4 (d, $^2J_{CP}$=25 Hz, P***C***H$_2$), 49.3 (d, $^2J_{CP}$=4 Hz, ***C***^{3}), 66.6 (d, $^3J_{CP}$=8 Hz, N***C***H), 99.5 (d, $^2J_{CP}$=26 Hz, ***C*^{1}**), 119.3 (d, $^2J_{CP}$=5 Hz, ***C*^{2}**), 124.2-141.5 (m, 24C, ***C***$_{arom}$). $^{31}P\{^1H\}$ NMR (202.5 MHz, CDCl$_3$): δ= 30.74 (s), -142.74 (hept, $^1J_{PF}$=716 Hz, PF_6^-). Minor *trans*-P Isomer (**4b**, 9%) : ^{1}H NMR: δ=1.26 (dd, 3H, $^3J_{HH}$=6.6 Hz, $^4J_{HP}$=9.5 Hz, ***C*^{4}*H*$_3$**), 2.92 (br d, $^3J_{HH}$=10.5 Hz, ***H*^{3a}**), 3.67 (dd, 1H, $^2J_{HH}$=2.4 Hz, ^3JH$_{3s}$H$_2$=6.2 Hz, ***H*^{3s}**), 4.05 (m, 1H, ***H*^{1a}**) 5.72 (dt, 1H, $^3J_{H2H3s}$=6.8 Hz, $^3J_{H2H1a}$=$^3J_{H2H3a}$=12.4 Hz, ***H*^{2}**), 6.22 (d, 1H, $^3J_{HH}$=10.9 Hz, N***H***). $^{13}C\{^1H\}$ NMR: δ=16.9 (d, $^3J_{CP}$=5 Hz, ***C*^{4}**), 30.6 (d, $^2J_{CP}$=24 Hz, P***C***H$_2$), 49.1 (broad, ***C***^{3}), 66.8 (d, $^3J_{CP}$=7 Hz, N***C***H), 103.3 (d, $^2J_{CP}$=27 Hz, ***C*^{1}**), 119.2 (d, $^2J_{CP}$=6 Hz, ***C*^{2}**). $^{31}P\{^1H\}$ NMR: δ= 28.90 (s). *cis*-P isomer (**4c**, 9%) : ^{1}H NMR: δ=1.62 (dd, 3H, $^3J_{HH}$=6.6 Hz, $^4J_{HP}$=9.0 Hz, ***C*^{4}*H*$_3$**), 3.52 (masked, ***H*^{1s}**), 3.84 (dd, 1H, $^3J_{HP}$=9.5 Hz, $^3J_{H1aH2}$=13.5 Hz, ***H*^{1a}**), 4.16 (masked, ***H*^{3a}**), 5.61 (dt, 1H, $^3J_{H2H3s}$=7.7 Hz, $^3J_{H2H1a}$=$^3J_{H2H3a}$=12.2 Hz, ***H*^{2}**), 6.41 (d, 1H, $^3J_{HH}$=10.9 Hz, N***H***). $^{13}C\{^1H\}$ NMR: δ= 19.6 (***C*^{4}**), 66.3 (d, $^3J_{CP}$=7 Hz, N***C***H), 72.6 (d, $^2J_{CP}$=4 Hz, ***C***^{3}), 76.3 (d, $^2J_{CP}$=27 Hz, ***C*^{1}**), 122.5 (d, $^2J_{CP}$=5 Hz, ***C*^{2}**). $^{31}P\{^1H\}$ NMR: δ= 28.35 (s). *cis*-P isomer (**4d**, 4%) : ^{1}H NMR: δ= 2.80 (masked, ***H***), 4.03 (masked,

H), 5.78 (dt, 1H, $^3J_{H2H3s}$=7.7 Hz, $^3J_{H2H1a}$=$^3J_{H2H3a}$=12.2 Hz, ***H²***), 5.83 (d, 1H, $^3J_{HH}$=10.9 Hz, N***H***). $^{31}P\{^1H\}$ NMR: δ= 25.44 (s).

[Pd(η³-CH₂CHCHPh)(Ph₂PCH₂CHPhNHPh),PF₆], (5)

Starting materials : [Pd(η³-PhC$_3$H$_4$)Cl]$_2$ (54 mg, 0.10 mmol), **L¹** (80 mg, 0.21 mmol) and NaPF$_6$ (43 mg, 0.26 mmol). Yield: 0.133 g (85%). $C_{35}H_{33}F_6NP_2Pd$ (750.0): Calculated: C 56.06, H 4.40, N 1.90; found: C 55.92, H 4.79, N 2.41. Major *trans*-P isomer (**5a**, 55%): ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ= 2.77 (d, 1H, $^3J_{HH}$=8.1 Hz, ***H³ᵃ***), 2.90 (t, 1H, $^2J_{HP}$=$^2J_{HH}$=14.6 Hz, PC***H***), 3.40 (t, 1H, $^2J_{HP}$=$^2J_{HH}$=13.9 Hz, PC***H***), 3.88 (m, 2H, NC***H*** and ***H³ˢ***), 5.82 (m, 2H, ***H²*** and ***H¹ᵃ***), 5.93 (d, 1H, $^3J_{HH}$=11.1 Hz, N***H***), 6.23-7.92 (m, merged with other diastereomers aromatic protons, ***H***$_{arom}$). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ= 37.1 (d, $^2J_{CP}$=24 Hz, P***C***H$_2$), 48.8 (***C³***), 69.7 (d, $^3J_{CP}$=10 Hz, N***C***H), 104.7 (d, $^2J_{CP}$=24 Hz, ***C¹***), 111.3 (d, $^2J_{CP}$=5 Hz, ***C²***), 120.8-142.9 (m, 30C, ***C***$_{arom}$). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ= 35.50 (s), -142.70 (hept, $^1J_{PF}$=716 Hz, PF_6^-). Minor *trans*-P isomer (**5b**, 22%): ^{1}H NMR: δ= 3.04 (d, 1H, $^3J_{HH}$=10.8 Hz, ***H³ᵃ***), 3.32 (m, 2H, PC***H***$_2$), 3.62 (d, 1H, $^3J_{HH}$= 5.9 Hz, ***H³ˢ***), 3.99 (m, NC***H***), 4.67 (t, 1H, $^3J_{HP}$=$^3J_{HH}$=9.9 Hz, ***H¹ᵃ***), 5.38 (d, 1H, $^3J_{HH}$=10.9 Hz, N***H***), 6.20 (m, ***H²***), 6.19-7.88 (m, merged with other diastereomers aromatic protons, ***H***$_{arom}$). $^{13}C\{^1H\}$ NMR: δ= 37.8 (d, $^2J_{CP}$=24 Hz, P***C***H$_2$), 49.8 (***C³***), 69.7 (d, $^3J_{CP}$=10 Hz, N***C***H), 104.6 (d, $^2J_{CP}$=24 Hz, ***C¹***), 115.0 (d, $^2J_{CP}$=5 Hz, ***C²***), 121.4-147.3 (***C***$_{arom}$). $^{31}P\{^1H\}$ NMR: δ= 33.45 (s). Isomer *cis*-P (**5c**, 12%): ^{1}H NMR: δ= 4.25 (t, 1H, $^3J_{HP}$=$^3J_{HH}$=7.2 Hz, ***H¹ˢ***), 4.47 (dd, 1H, $^3J_{HH}$=9.9 Hz, $^3J_{HP}$=13.6 Hz, ***H¹ᵃ***), 4.81 (d, 1H, $^3J_{HH}$=11.5 Hz, ***H³ᵃ***), 6.19 (masked, ***H²***). $^{13}C\{^1H\}$ NMR: δ= 36.3 (d, $^2J_{CP}$=25 Hz, P***C***H$_2$), 67.7 (d, $^3J_{CP}$=10 Hz, N***C***H), 73.9 (d, $^2J_{CP}$=5 Hz, ***C³***), 80.7 (d, $^2J_{CP}$=26 Hz, ***C¹***), 116.7 (d, $^2J_{CP}$=5 Hz, ***C²***). $^{31}P\{^1H\}$ NMR: δ= 25.86 (s). Isomer *cis*-P (**5d**, 11%): ^{1}H NMR: δ= 3.08 (dd, 1H, $^3J_{HH}$=9.4 Hz, $^3J_{HP}$=13.7 Hz, ***H¹ᵃ***), 3.85 (masked, ***H³ˢ***), 4.62 (d, 1H, $^3J_{HH}$=11.5 Hz, ***H³ᵃ***), 5.83 (masked, ***H²***). $^{13}C\{^1H\}$ NMR: δ= 36.3 (d, $^2J_{CP}$=25 Hz, P***C***H$_2$), 68.1 (d, $^3J_{CP}$=10 Hz, N***C***H), 74.6 (d, $^2J_{CP}$=5 Hz, ***C³***), 82.0 (d, $^2J_{CP}$=25 Hz, ***C¹***), 119.6 (d, $^2J_{CP}$=5 Hz, ***C²***). $^{31}P\{^1H\}$ NMR: δ= 25.61 (s).

[Pd(η³-CH₂CHCHPh)(Ph₂PCH₂CHPhNH(2,6-C₆H₃(ⁱPr)₂),PF₆], (6)

Starting materials : [Pd(η³-PhC$_3$H$_4$)Cl]$_2$ (64 mg, 0.12 mmol), **L²** (115 mg, 0.25 mmol) and NaPF$_6$ (81 mg, 0.48 mmol). Suitable yellow crystals for X-Ray diffraction were obtained from dichloromethane by layering with pentane. Yield: 0.172 g (82%). $C_{41}H_{46}F_6NP_2Pd$ (835.2): Calculated: C 58.96, H 5.55, N 1.67; found C 59.19, H 5.78, N 1.94%. Major *cis*-P isomer (**6c**, 63%): ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ= 0.32 (d, 3H, $^3J_{HH}$=6.4 Hz, CH-(C***H***$_3$)$_2$), 0.61 (d, 3H, $^3J_{HH}$=6.7 Hz, CH-(C***H***$_3$)$_2$), 1.11 (d, 3H, $^3J_{HH}$=6.7 Hz, CH-(C***H***$_3$)$_2$), 1.17 (d, 3H, $^3J_{HH}$=6.5 Hz, CH-

(C***H***$_3$)$_2$), 2.86 (h, 1H, $^3J_{HH}$=6.7 Hz, C***H***-(CH$_3$)$_2$), 3.02 (dt, 1H, $^3J_{HH}$=2.8 Hz, $^2J_{HP}$=$^2J_{HH}$=14.8 Hz, PC***H***), 3.41 (m, 1H, C***H***-(CH$_3$)$_2$), 3.66 (dt, 1H, $^3J_{HH}$=3.4 Hz, $^2J_{HP}$=$^2J_{HH}$=14.8 Hz, PC***H***), 3.83 (dd, 1H, $^3J_{HP}$=6.1 Hz, $^3J_{HH}$=7.8 Hz, ***H^{1s}***), 3.97 (m, 1H, NC***H***), 4.41 (dd, 1H, $^3J_{HP}$=8.8 Hz, $^3J_{H1aH2}$=13.8 Hz, ***H^{1a}***), 4.79 (d, 1H, $^3J_{HH}$=11.8 Hz, ***H^{3a}***), 6.20 (ddd, 1H, $^3J_{H2H1s}$=7.9 Hz, $^3J_{H2H3a}$=11.8 Hz, $^3J_{H2H1a}$=13.7 Hz, ***H^{2}***), 6.62 (d, 1H, $^3J_{HH}$=10.8 Hz, N***H***), 6.79-7.79 (m, merged with other diastereomers aromatic protons, ***H***$_{arom}$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$): δ= 23.0 (CH-(***C***H$_3$)$_2$), 23.8 (CH-(***C***H$_3$)$_2$), 25.8 (CH-(***C***H$_3$)$_2$), 25.9 (CH-(***C***H$_3$)$_2$), 27.9 (*C*H-(**C**H$_3$)$_2$), 29.5 (***C***H-(CH$_3$)$_2$), 35.2 (d, $^2J_{CP}$=24 Hz, P***C***H$_2$), 67.0 (d, $^3J_{CP}$=8 Hz, N***C***H), 74.6 (d, $^2J_{CP}$=6 Hz, ***C^{3}***), 79.4 (d, $^2J_{CP}$=25 Hz, ***C^{1}***), 116.4 (d, $^2J_{CP}$=5 Hz, ***C^{2}***), 124.7-140.8 (m, 30C, ***C***$_{arom}$). ^{31}P{^{1}H} NMR (202.5 MHz, CDCl$_3$): δ= 21.85 (s), -142.62 (hept, $^1J_{PF}$=716 Hz, PF_6^-). Minor *cis*-P isomer (**6d**, 22%): ^{1}H NMR: δ= 0.28 (d, 3H, $^3J_{HH}$=6.4 Hz, CH-(C***H***$_3$)$_2$), 0.70 (d, 3H, $^3J_{HH}$=6.7 Hz, CH-(C***H***$_3$)$_2$), 1.20 (d, 3H, $^3J_{HH}$=6.6 Hz, CH-(C***H***$_3$)$_2$), 1.27 (d, 3H, $^3J_{HH}$=6.7 Hz, CH-(C***H***$_3$)$_2$), 2.80 (h, 1H, $^3J_{HH}$=6.7 Hz, C***H***-(CH$_3$)$_2$), 2.99 (m, 2H, PC***H*** and ***H^{3s}***), 3.52 (dt, 1H, $^3J_{HH}$=3.6 Hz, $^2J_{HP}$=$^2J_{HH}$=14.7 Hz, PC***H***), 3.78 (m, 1H, C***H***-(CH$_3$)$_2$), 4.05 (m, 1H, NC***H***), 4.23 (t, 1H, $^3J_{HP}$=$^3J_{HH}$=7.3 Hz, ***H^{1s}***), 4.86 (d, 1H, $^3J_{HH}$=11.8 Hz, ***H^{3a}***), 6.40 (m, 1H, ***H^{2}***), 6.44 (d, 1H, $^3J_{HH}$=10.7 Hz, N***H***), 6.85-7.79 (m, merged with other diastereomers aromatic protons, ***H***$_{arom}$). ^{13}C{^{1}H} NMR: δ= 23.3 (CH-(***C***H$_3$)$_2$) 24.6 (CH-(***C***H$_3$)$_2$), 25.6 (CH-(***C***H$_3$)$_2$), 25.9 (CH-(***C***H$_3$)$_2$), 28.0 (***C***H-(CH$_3$)$_2$), 29.4 (***C***H-(CH$_3$)$_2$), 35.5 (d, $^2J_{CP}$=21 Hz, P***C***H$_2$), 66.5 (d, $^3J_{CP}$=8 Hz, N***C***H), 76.1 (d, $^2J_{CP}$=5 Hz, ***C^{3}***), 76.6 (d, $^2J_{CP}$=27 Hz, ***C^{1}***), 118.8 (d, $^2J_{CP}$=6 Hz, ***C^{2}***), 124.8-141.0 (***C***$_{arom}$). ^{31}P{^{1}H} NMR: δ= 29.68 (s). Isomer *trans*-P (**6a**, 9%): ^{1}H NMR: δ= 2.79 (d, 1H, $^3J_{HH}$=11.9 Hz, ***H^{3a}***), 3.62 (d, 1H, $^3J_{HH}$= 6.8 Hz, ***H^{3s}***), 5.68 (dt, 1H, $^3J_{HH}$=7.0 Hz, $^3J_{HH}$=11.9 Hz, ***H^{2}***), 5.95 (dt, 1H, $^3J_{HH}$=8.9 Hz, $^3J_{HP}$= 13.7 Hz, ***H^{1a}***). ^{31}P{^{1}H} NMR: δ= 31.60 (s). Isomer *trans*-P (**6b**, 7%): ^{1}H NMR: δ= 2.84 (masked, ***H^{3a}***), 4.92 (dt, 1H, $^3J_{HH}$=9.9 Hz, $^3J_{HP}$= 13.7 Hz, ***H^{1a}***), 6.40 (masked, ***H^{2}***). ^{31}P{^{1}H} NMR: δ= 32.33 (s).

Crystal structure determination for 6.

Crystal data and refinement figures are reported in Table 3. The data set was collected on an Enraf-Nonius KappaCCD diffractometer at 110 K using Mo Kα radiation. The structure was solved via a Patterson search program[61] and refined with full-matrix least-squares methods[62] based on |F^2| with the aid of the WINGX program[63]. The allylic fragment (CH$_2$···CH···CHPh) was found to be disordered with two different orientations (*endo/exo*). The occupation factors refined to m1=0.78 (*endo* isomer) and m2=1-m1=0.22 (*exo* isomer). All non-hydrogen atoms were refined with anisotropic thermal parameters except for the atoms belonging to the minor allylic fragment (*exo*) and the terminal carbon atom, C(1), of the major allylic fragment. The positions of the hydrogen atoms were either calculated or located on final Fourier difference maps and refined, after

idealization, with a riding model with isotropic temperature factors fixed to 1.5 or 1.2 times those of the corresponding parent atoms. CCDC-218899 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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Captions of Figures, Schemes and Tables

Figure 1: Regioselectivity and enantioselectivity in palladium-catalyzed allylic alkylation arising from different diastereomeric η^3-allyl complexes

Figure 2: Coordinative features of aminophosphine **L^1** in neutral and cationic allyl palladium complexes

Figure 3: High field ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 283 K) of the CH_3 terminal group pf complex **3**, showing the presence of four isomers

Figure 4: Schematic representation and distribution of complexes **3-6** isomers

Figure 5: ORTEP views of the *exo* **6c** and *endo* **6d** isomers. Only relevant hydrogen atoms are shown. For clarity, the CH_2Cl_2 solvent and the hexafluorophosphate anion are omitted.

Figure 6: Kinetic ^{31}P NMR monitoring of crystals of **6** dissolved in $CDCl_3$

Figure 7: The ^{1}H-^{1}H phase-sensitive NOESY spectrum ($CDCl_3$, 500 MHz, 293 K) of complex **1**, showing the exchange cross-peaks (labelled *a* to *d*) in the isomers **1a** and **1b**.

Figure 8: Exchange allyl protons between isomers **1a** and **1b**

Table 1: ^{13}C NMR data for allylic carbon atoms in complexes **1** and **2**

Table 2: Selected ^{13}C and ^{1}H NMR datas for allylic complexes **3-6**

Table 3: Crystallographic and Refinement data for complexes **6**

Table 4: Selected bond lengths [Å] and bond angles [°] for **6c** and **6d**

Scheme 3: η^3-η^1-η^3 isomerization pathways involving a selective *trans*-P opening. Dotted square: only for substituted allyl complexes **3-6**

Figure 1

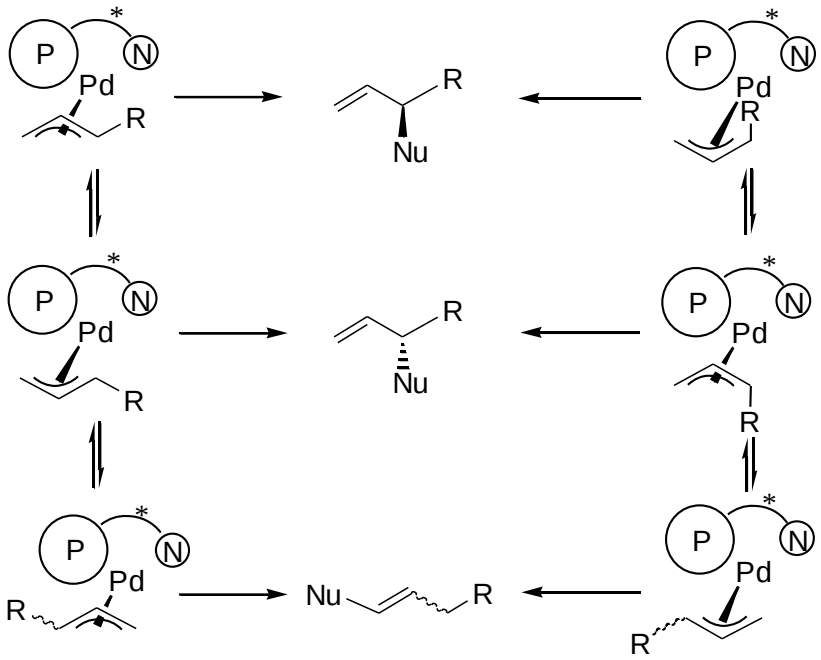


Figure 2

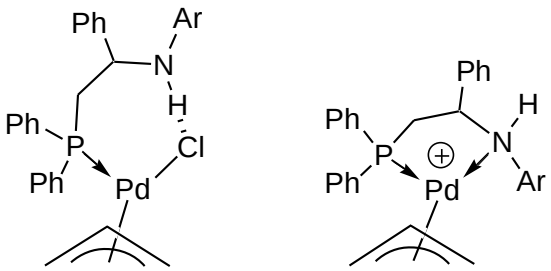


Figure 3

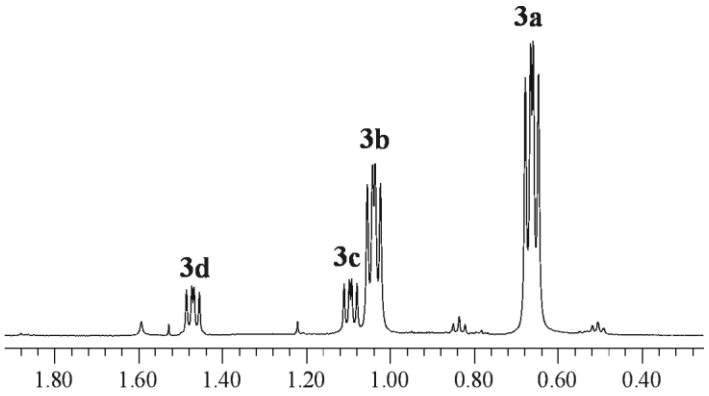


Figure 4

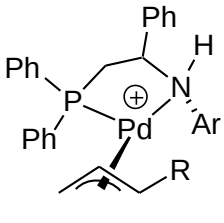
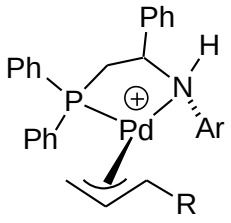
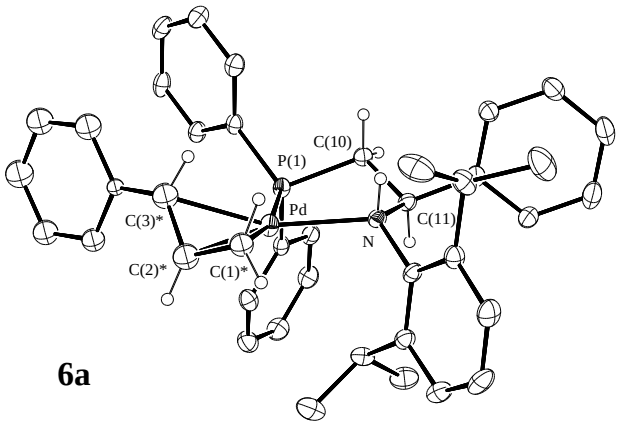
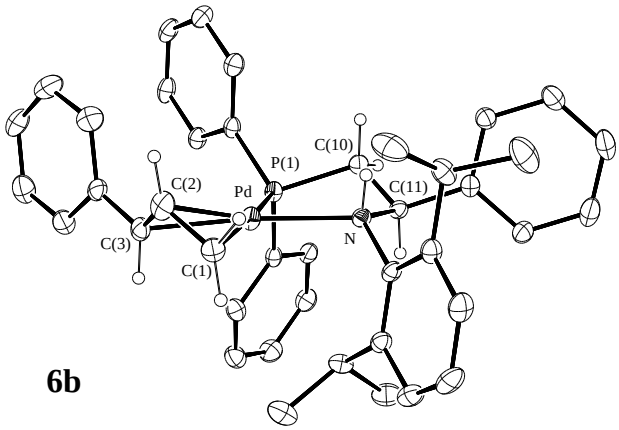
	 *endo*/*exo syn trans*-P (**a**/**b** or **b**/**a**)	 *endo*/*exo syn cis*-P (**c**/**d** or **d**/**c**)
3	53/30	11/6
4	78/9	9/4
5	55/22	12/11
6	9/7	62/22

Figure 5



6a



6b

Figure 6

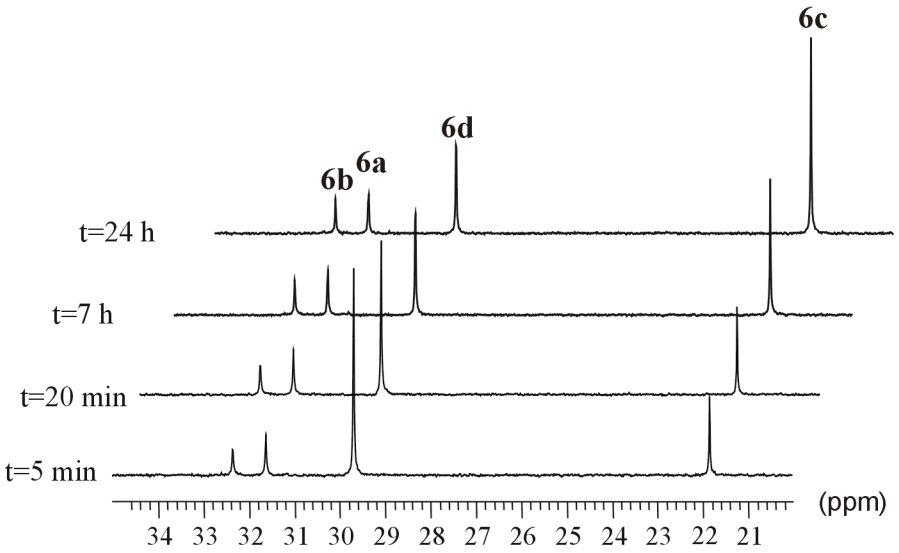

6c
6d
6a
6b
t=24 h
t=7 h
t=20 min
t=5 min
(ppm)
34 33 32 31 30 29 28 27 26 25 24 23 22 21

Figure 7

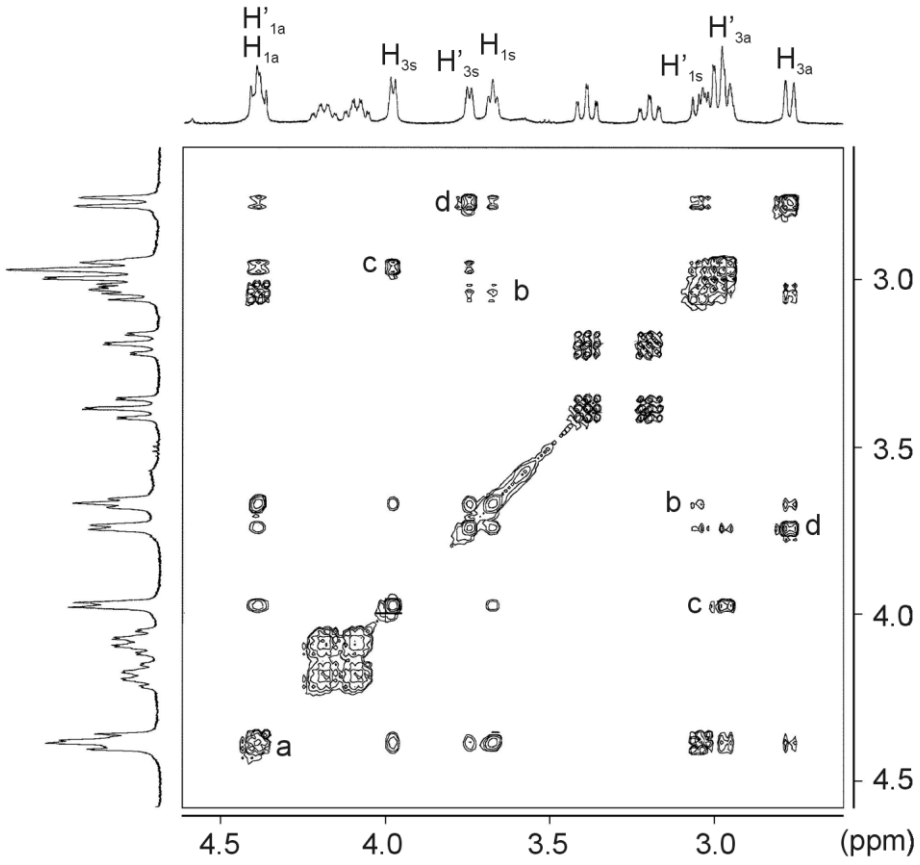
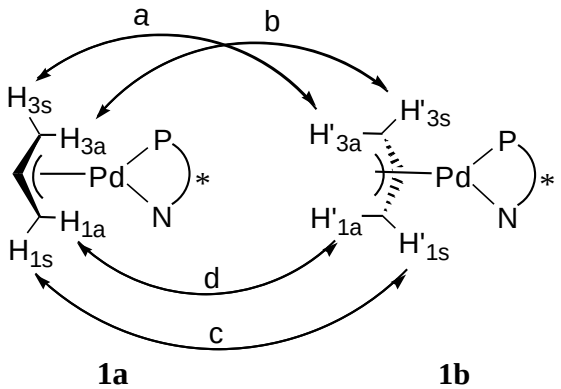
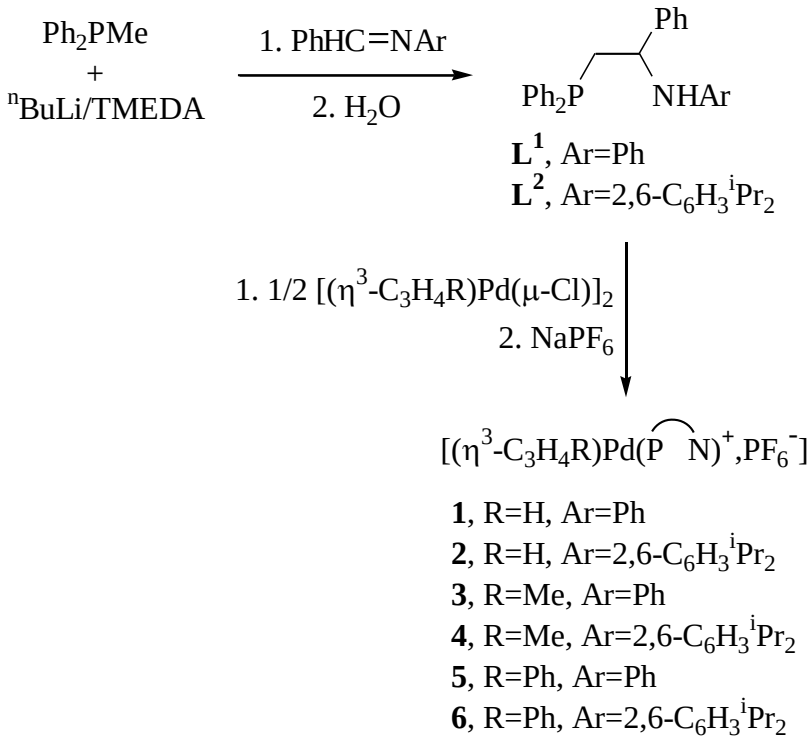


Figure 8

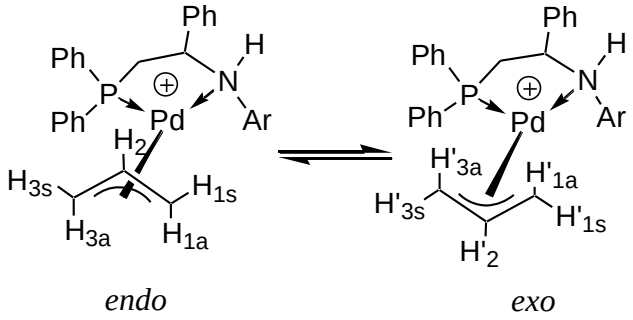


1a **1b**

Scheme 1



Scheme 2



endo *exo*

Scheme 3

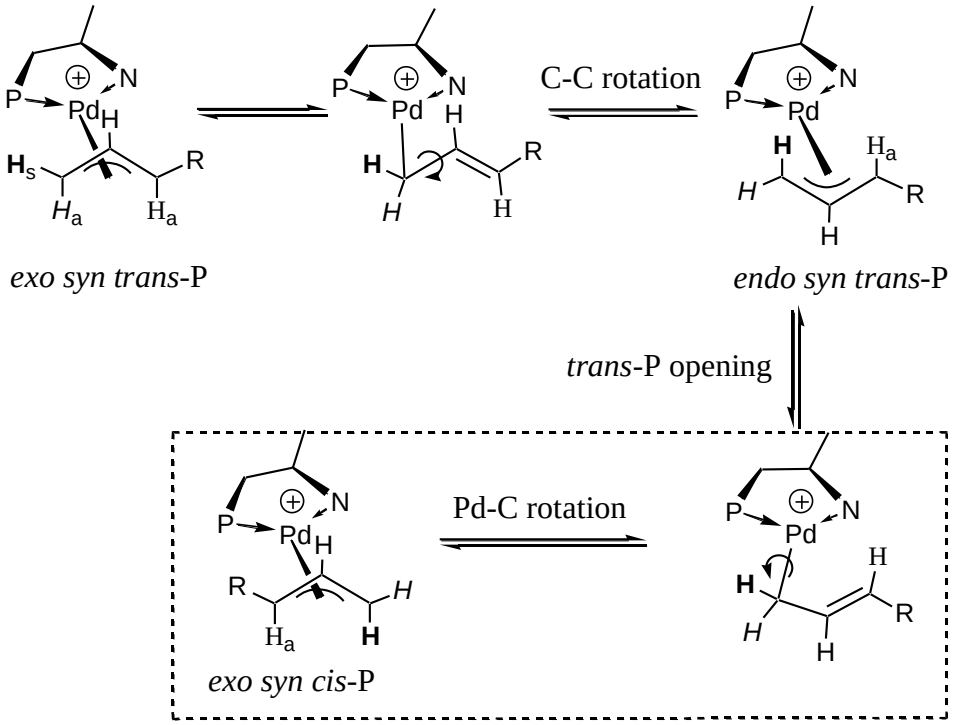


Table 1

	$\delta^{13}C$ ($^2J_{HP}$ in Hz)			$\Delta\delta^{13}C$
	$C_{1\ transP}$	C_2	$C_{3\ cisP}$	(δC_1-δC_3)
1a	87.1 (27)	120.6	51.4	35.7
1b	84.6 (28)	123.0	52.1	32.5
2a	82.3 (27)	120.3 (5)	52.4	29.9
2b	80.6 (29)	122.2 (5)	53.4	27.2

Table 2

	$\delta^{13}C$ (J_{PC} in Hz)				$\delta^{1}H$ (J_{HP} in Hz)					
Complexes	C_1	C_2	C_3	CH_3	H_{1anti}	H_{1syn}	H_2	H_{3syn}	H_{3anti}	CH_3
3a 53%	102.9 (26)	116.2 (5)	46.7 (4)	14.1 (4)	4.98 (ind)	-	5.23	3.79	2.56	0.66 (9.3)
3b 30%	101.7 (26)	118.9 (5)	47.5 (3)	14.2 (4)	3.92 (ind)	-	5.58	3.54	2.82	1.04 (9.1)
3c 11%	78.3 (23)	123.5 (6)	72.3 (5)	17.2	4.17 (ind)	2.72 (ind)	5.73	-	3.85	1.09 (9.1)
3d 6%	74.2 (25)	ind	69.2 (4)	18.0	ind	2.81 (ind)	5.68	-	ind	1.46 (9.1)
4a 78%	99.5 (26)	119.3 (5)	49.3 (4)	15.7 (4)	4.75 (ind)	-	5.34	4.10	2.83	0.67 (9.4)
4b 9%	103.3 (27)	119.2 (6)	49.1	16.9 (5)	4.05 (ind)	-	5.72	3.67	2.92	1.26 (9.5)
4c 9%	76.3 (27)	122.5 (5)	72.6 (4)	19.6	3.84 (9.4)	3.52 (ind)	5.61	-	4.16	1.62 (9.0)
4d 4%	ind	ind	ind	19.0	ind	ind	5.83	-	ind	ind
5a 55%	104.7 (24)	111.3 (5)	48.8	-	5.82 (ind)	-	5.82	3.88	2.77	-
5b 22%	104.6 (24)	115.0 (5)	49.8	-	4.67 (9.9)	-	6.20	3.62	3.04	-
5c 12%	80.7 (26)	116.7 (5)	73.9 (5)	-	4.47 (9.2)	4.25 (7.2)	6.19	-	4.81	-
5d 11%	82.0 (25)	119.6 (5)	74.6 (5)	-	3.08 (9.3)	3.85 (ind)	5.83	-	4.62	-
6a 9%	ind	ind	ind	-	5.95 (9.0)	-	5.68	3.62	2.79	-
6b 7%	ind	ind	ind	-	4.92 (9.9)	-	6.40	ind	2.84	-
6c 62%	79.4(25)	116.4(5)	74.6(6)	-	4.41(8.8)	3.83(7.8)	6.20	-	4.79	-
6d 22%	76.6 (27)	118.8 (6)	76.1 (5)	-	2.99 (ind)	4.23 (7.3)	6.40	-	4.86	-

Table 3

Formula	$C_{41}H_{45}NPPd \cdot PF_6 \cdot 0.5(CH_2Cl_2)$
M	876.58
T; K	110(2)
Crystal system	monoclinic
Space group	C2/c
a; Å	13.8841(2)
b; Å	17.5047(2)
c; Å	33.1026(5)
β; deg	95.590(1)
V; Å^3	8006.9(2)
Z	8
F(000)	3592
D_{calc}; g/cm^3	1.454
diffractometer	Enraf-Nonius KappaCCD
scan type	mixture of ϕ rotations and ω scans
λ; Å	0.71073
μ; mm^{-1}	0.669
Crystal size; mm^3	0.35 x 0.25 x 0.20
sin(θ)/λ max; Å^{-1}	0.65
Index ranges	h: -17; 18 k: -21; 22 l: -42; 42
Absorption correction	SCALEPACK
RC = Refl. Collected	16441
IRC = independent RC	9042 [R(int) = 0.032]
IRCGT = IRC and [I>2σ(I)]	6538
Refinement method	Full-matrix L.S. on F^2
Data / restraints / parameters	9042 / 9 / 506
R for IRCGT	R1[a] = 0.0419, wR2[b] = 0.0938
R for IRC	R1[a] = 0.0697, wR2[b] = 0.1032
Goodness-of-fit[c]	1.067
Largest diff. peak and hole; e.Å^{-3}	0.80 and −1.10

[a] $R1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. [b] $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]^{1/2}$ where $w=1/[\sigma^2(Fo^2)+(0.045P)^2+4.95P]$ where $P=(Max(Fo^2,0)+2*Fc^2)/3$

[c] Goodness of fit $=[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$.

Table 4

	Endo		*exo*
Pd-N	2.165(2)		
Pd-P(1)	2.2839(7)		
Pd-C(1)	2.187(4)	Pd-C(1*)	2.223(16)
Pd-C(2)	2.153(4)	Pd-C(2*)	2.11(2)
Pd-C(3)	2.156(4)	Pd-C(3*)	2.214(15)
C(1)-C(2)	1.418(6)	C(1*)-C(2*)	1.461(16)
C(2)-C(3)	1.413(6)	C (2*)-C(3*)	1.415(15)
N-Pd-P(1)	84.89(6)		
C(1)-Pd-C(3)	67.31(16)	C(1*)-Pd-C(3*)	65.0(5)
N-Pd-C(1)	101.91(13)	N-Pd-C(1*)	101.6(4)
P(1)-Pd-C(3)	105.82(10)	P(1)-Pd-C(3*)	104.5(3)
C(1)-C(2)-C(3)	116.5(5)	C(1*)-C(2*)-C(3*)	111.9(15)
C(2)-C(3)-C(4)	123.9(4)	C(2*)-C(3*)-C(4*)	129.2(16)

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