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# Synthesis and characterization of palladium(II) complexes with chiral aminophosphine ligands: Catalytic behaviour in asymmetric hydrovinylation. Crystal structure of *cis*-[$PdCl_2$(PPh((*R*)-NHCHC$H_3$Ph)$_2$)$_2$]

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**Abstract**

Optically active ligands of type $Ph_2PNHR$ (R = (*R*)-$CHCH_3Ph$, (**a**); (*R*)-$CHCH_3Cy$, (**b**); (*R*)-$CHCH_3$Naph, (**c**)) and $PhP(NHR)_2$ (R = (*R*)-$CHCH_3Ph$, (**d**); (*R*)-$CHCH_3Cy$, (**e**)) with a stereogenic carbon atom in the R substituent were synthesized. Reaction with [$PdCl_2(COD)_2$] produced [$PdCl_2P_2$] (**1**) (P = $PhP(NHCHCH_3Ph)_2$), whose molecular structure determined by X-ray diffraction showed *cis* disposition for the ligands. All nitrogen atoms of amino groups adopted *S* configuration. The new ligands reacted with allylic dimeric palladium compound [Pd($\eta^3$-2-methylallyl)Cl]$_2$ to gave neutral aminophosphine complexes [Pd($\eta^3$-2-methylallyl)ClP] (**2a**–**2e**) or cationic aminophosphine complexes [Pd($\eta^3$-2-methylallyl)$P_2$]$BF_4$ (**3a**–**3e**) in the presence of the stoichiometric amount of $AgBF_4$. Cationic complexes [Pd($\eta^3$-2-methylallyl)(N$CCH_3$)P]$BF_4$ (**4a**–**4e**) were prepared in solution to be used as precursors in the catalytic hydrovinylation of styrene. $^{31}$P NMR spectroscopy showed the existence of an equilibrium between the expected cationic mixed complexes **4**, the symmetrical cationic complexes [Pd($\eta^3$-2-methylallyl)$P_2$]$BF_4$ (**3**) and [Pd($\eta^3$-2-methylallyl)(N$CCH_3$)$_2$]$BF_4$ (**5**) coming from the symmetrization reaction. The extension of the process was studied with the aminophosphines (**a**–**e**) as well as with nonchiral monodentate phosphines ($PCy_3$ (**f**), $PBn_3$ (**g**), $PPh_3$ (**h**), $PMe_2Ph$ (**i**)) showing a good match between the extension of the symmetrization and the size of the phosphine ligand. We studied the influence of such equilibria in the hydrovinylation of styrene because the behaviour of catalytic precursors can be modified substantially when prepared '*in situ*'. While compounds **3** and bisacetonitrile complex **5** were not active as catalysts, the [Pd($\eta^3$-2-methylallyl)($\eta^2$-styrene)$_2$]$^+$ species formed in the absence of acetonitrile showed some activity in the formation of codimers and dimers. Hydrovinylation reaction between styrene and ethylene was tested using catalytic precursors solutions of [Pd($\eta^3$-2-methylallyl)LP]$BF_4$ ionic species (L = $CH_3CN$ or styrene) showing moderate activity and good selectivity. Better activities but lower selectivities were found when L = styrene. Only in the case of the precursor containing $Ph_2PNHCHCH_3Ph$ (**a**) ligand was some enantiodiscrimination (10%) found.


*Keywords:* Chiral aminophosphine ligands; Allylic palladium (II) complexes; Symmetrization reaction; Hydrovinylation reaction

## 1. Introduction

The catalytic asymmetric hydrovinylation of olefins is an important stereoselective carbon–carbon bond-forming reaction in organic synthesis [1]. The reaction is catalyzed by a variety of transition metal compounds being

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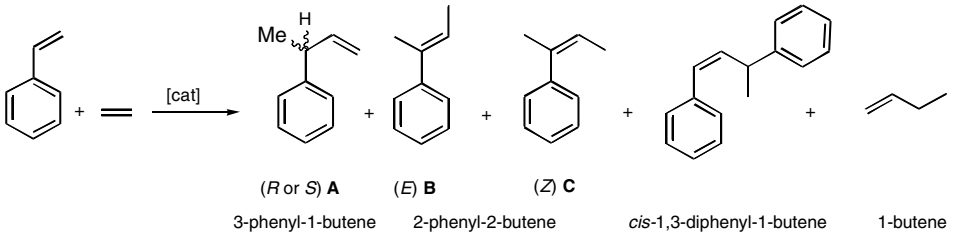
nickel and palladium the most frequently used. The scope of the reaction is limited by the nature of the olefin since excellent stereoselectivity is achieved only with conjugated dienes, strained olefins or intramolecular reactions [2]. The catalytic cycle proposed on nickel and palladium systems shows that the active catalyst is most likely an unsaturated phosphine-stabilized metal-hydride. Allylic precursors stabilized with one monodentate phosphine proved to be very useful since cleavage of the allyl substituent leads to the actual catalyst that initiates the heterodimerization. The model reaction of the process involves codimerization between styrene or vinylnaphtalene and ethylene (Eq. (1)). When these types of vinylarenes are used as prochiral olefins, the excellent regioselectivities obtained originate in the allylic nature of the intermediate.




(1)

However the control of the enantioselectivity of the reaction is more difficult. Very good enantioselectivities were initially obtained by Wilke [3] and more recently by the groups of Vogt [4], Gibson [5], Rajanbabu [6,7], Leitner [8] and Zhou [9] using phosphines, planar chromium phosphines, phosphinites, or phosphoramidites as stabilizing ligands with nickel and palladium systems. We investigated the model reaction using nickel and palladium precursors. The initial work provided evidence of the blocking effect of inert bidentate ligands [10]. Further research with allylic palladium precursors containing *P*-stereogenic phosphines enabled the enantioselective version of the process to be studied [11,12].

Synthesis of ligands with specific electronic and steric requirements is an essential part of an asymmetric catalysis program that relies on ligand tuning to bring about optimum results. Although there now exists a huge body of work on the chemistry of both phosphines and phosphites, aminophosphines containing P–N bonds instead of P–C or P–O bonds have received a lower level of attention. One potential reason for the underdevelopment of this chemistry is that the P–N bond is envisaged as being susceptible to relatively easily cleavage [13] but several new classes of P–O and P–N bond containing phosphorous ligands of high stability have been demonstrated to be capable of the acceleration and asymmetric catalysis of a number of synthetic organic reactions [14]. Moreover, these ligands may be constructed in large quantities through the use of relatively simple condensation processes, and from commercial starting materials. Woolins and coworkers have reported a number of examples of aminophosphines including these derived from 1,2-diaminobenzene [15], aminopyridine [16] and several diamines [17]. Burrows has reported the synthesis of ether functionalized aminophosphines [18] and aminophosphines derived from methyl benzyl amine are also well documented [19]. There are indications of the potential utility of transition metal complexes with aminophosphines. For example rhodium (I) [20] and platinum (II) [21] complexes of chiral aminophosphines have proved to be efficient catalysts for asymmetric hydrogenation and hydroformylation reactions respectively, and nickel complexes have been employed in the cyclodimerization of buta-1,3-diene [22]. Some preliminary studies on the use of bidentate aminophosphine ligands in palladium catalysed allylic alkylation reactions are reported [23].

We decided to focus the work on the synthesis of cationic allylic palladium (II) complexes with chiral monoamino and bisaminoarylphosphines containing one stereogenic carbon atom in the amino substituent, and use them as catalytic precursors for hydrovinylation asymmetric reaction. It is well known that the factors determining the discrimination ability of the ligands in this process remain poorly defined. The final efficiency of the reaction is determined by the delicate competition between the olefins present as well as all the species contained in the reaction medium. The fully characterization of the precursors solutions indicate that the cationic allylic palladium (II) complexes undergo symmetrization leading to mixtures of three different species

$$2[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_5)PL]^+ \rightleftharpoons [Pd(\eta^3\text{-}2\text{-}CH_3C_3H_5)P_2]^+ + [Pd(\eta^3\text{-}2\text{-}CH_3C_3H_5)L_2]^+ \quad (2)$$

The relative amount of each one, using different tertiary phosphines and aminophosphines, seems related to the steric parametres of the phosphine ligands. We evaluated the behaviour of each one in the catalytic hydrovinylation process.

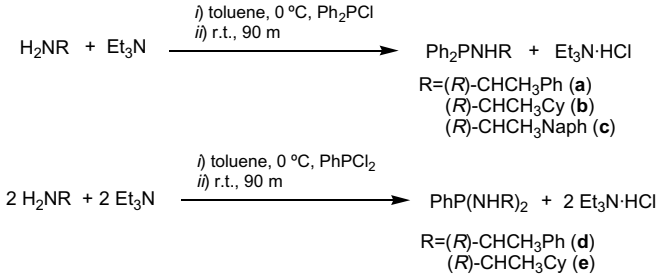
## 2. Results and discussion

### 2.1. Synthesis and characterization of the aminophosphines (*a*–*e*)

The monoaminophosphines $Ph_2P(NHR)$ were conveniently prepared as reported in the literature [19,24] through the reaction of chlorodiphenylphospine with the chiral primary amines $NH_2R$ (R = (*R*)-$CHCH_3Ph$ (**a**), (*R*)-$CHCH_3Cy$ (**b**), (*R*)-$CHCH_3Naph$ (**c**)) in the presence of triethylamine. Bisaminophosphines $PhP(NHR)_2$ (R = (*R*)-$CHCH_3Ph$ (**d**), (*R*)-$CHCH_3Cy$ (**e**)) were prepared by the same way but starting from the dichlorophenylphosphine and the stoichiometric amount of the primary amine [25] (Scheme 1).

Aminophosphines (**a**–**e**) were isolated as spectroscopically pure colourless oils in very good yields (80–90%) and can be stored for a long time under inert atmosphere. Relevant NMR data are shown in Table 1.

$^{31}P$ NMR shows that all compounds exhibit a single signal and the chemical shift increases from 36 ppm to 59 ppm depending on the presence of one or two amino groups bonded to the phosphorus atom but does not change with the different substituents on the amino group (phenyl, cyclohexyl and naphthyl). The observed chemical shift values compared with those for $PPh_3$ (−5 ppm) and for the trisaminophosphine $P(NHCHCH_3Ph)_3$ (104.8 ppm) depicted by Kolodiaznyi and Prynada [25] suggest less basicity and bigger cone angle [26] when substitution increases. $^1H$–$^{13}C$ heterocorrelation NMR experiment allowed us to assign $^1H$ NMR spectra unequivocally. $^1H$ spectra of monoaminophosphine ligands (**a**, **b** and **c**) show a broad singlet for the aminic hydrogen, a multiplet for methinic proton and a doublet for the methyl proton of the amino group. $^1H$ spectra of the bisaminophosphine ligands (**d**, **e**) show two signals for $CH_3$ groups coupled to the methinic proton, two complex multiplets for the CH proton and two different broad signals for the NH proton of amino groups coupled to the phosphorus atom as confirmed by $^1H$–{$^{31}P$} experiments. It has been noted that hindered rotation about the P–N bond may exist as reported in the literature [27]. It is known that monoaminophosphines and bisaminophosphines bearing primary amino groups exist in tautomeric equilibrium with PH-iminophosphines and that bisaminophosphines also are amenable to condensation [27]. NMR spectra allowed us to observe that freshly prepared samples did not contain significant amounts of condensation products and that the position of the prototropic equilibrium is displaced significantly towards the NH form.




Scheme 1.

### 2.2. Synthesis and characterization of the palladium (II) complexes

#### 2.2.1. Neutral complex cis-[$PdCl_2$(PPh((*R*)-NHCH-$CH_3Ph)_2)_2$] (*1*)

The reaction of two equivalents of bisaminophosphine (**d**) with [$PdCl_2$(COD)] in dichloromethane gave nearly quantitative yields of [$PdCl_2P_2$] (**1**). The $^{31}P$ NMR spectrum of the palladium complex showed one phosphorus resonance at 57.1 ppm according to the formation of only one isomer. $^1H$ NMR spectrum showed two different doublets for the methyl group, two doublet of doublets for the aminic protons and two multiplets for CH protons as shown in Table 1, according to the nonequivalence of the two aminosubstituents of the same phosphorus atom observed in the free phosphine. NOESY experiment allowed a complete assignment of the protons of each amino group; NOE contacts between protons at 4.8, 3.5 and 1.14 ppm and between protons at 3.26, 4.6 and 1.37 ppm indicate that each set belongs to different amino group of the same phosphine ligand.

Table 1
Selected NMR data[a] ($\delta$ ppm, in $CDCl_3$, 298 K) for aminophosphine ligands (**a**–**e**) and [$PdCl_2$($PhP(NHCHCH_3Ph)_2$)$_2$] (**1**) complex

| Compound | $\delta^{31}P$ | $\delta^1H$(N*H*) | $\delta^1H$(C*H*) | $\delta^1H$(C*H*$_3$) |
|---|---|---|---|---|
| $Ph_2PNHCHCH_3Ph$ (**a**) | 36.0 (s) | 2.18 (bs) | 4.22 (m) | 1.39 (d; 7.0) |
| $Ph_2PNHCHCH_3Cy$ (**b**) | 36.4 (s) | 1.70–1.55 | 2.93 (m) | 1.06 (d; 6.8) |
| $Ph_2PNHCHCH_3Naph$ (**c**) | 36.5 (s) | 2.26 (bs) | 5.02 (m) | 1.52 (d; 7.0) |
| $PhP(NHCHCH_3Ph)_2$(**d**) | 59.1 (s) | 2.42 (bd; 6.7) | 4.18–4.02 | 1.31 (d; 6.6) |
| | | 2.53 (bt; 7.2) | | 1.48 (d; 6.6) |
| $PhP(NHCHCH_3Cy)_2$ (**e**) | 60.7 (s) | 2.05 (bd; 8.2) | 3.05–2.97 | 1.11(pt; 6.0) |
| | | 1.92 (bd; 6.7) | | |
| [$PdCl_2P_2$] (**1**) | 57.1 (s) | 4.80 (dd; 11.6, 9.6) | 3.50 (m) | 1.14 (d; 7.2) |
| | | 3.26 (dd; 9.2, 5.6) | 4.6 (m) | 1.37 (d; 6.8) |

[a] Multiplicity: s, singlet; d, doublet; t, triplet; pt, pseudotriplet; m, multiplet; b, broad signal. Coupling constant are given in Hz and are shown in parentheses after the multiplicity. $^1H$ NMR: 400 Hz. $^{31}P$–{$^1H$} NMR: 100.56 Hz.

Recrystallization from $CH_2Cl_2$/hexane mixture gave orange crystals of $[PdCl_2P_2]$ (**1**) suitable for X-ray analysis. The crystal structure indicate the *cis* geometry of the ligands and retention of the *R* configuration for the stereogenic amine carbon atom. All stereogenic nitrogen atoms show the same *S* configuration. Selected bond lengths and angles are given in Table 2, and molecular structure is shown in Fig. 1.

The metallic centre is distorted square-planar, with *cis* angles values shown in Table 2. The P–N distances are shorter than the generally accepted range for P–N single bond (e.g. 1.689–1.727 Å in piperidinophosphines [28]), suggesting a degree of double bond character as described [18a]. This situation is generally observed in complexes of aminophosphines, and a search of the Cambridge Structural Database revealed the average P–N distance for aminophosphines of type $Ph_2NHR$ (R = alkyl or aryl) to be 1.67 Å (range 1.63–1.73 Å) [25]. A significant π-stacking interaction involves the phenyl rings bonded to the phosphorus atom; the dihedral angle between the mean planes of the π-stacked aromatic rings is 10.7(2)° and the distance between the centre of the rings is 3.866 Å. The existence of this π-stacking interaction may favour the presence of the *cis* isomer exclusively. The values of the angles around the nitrogen atoms are consistent with significant $sp^2$ character in good agreement with the partial double bond character of the P–N bond. The structure of the complex shows the presence of an intramolecular hydrogen bond between N(2) aminic proton and the chloride ligand Cl(2) (2.54(2) Å), as well as between the N(3) aminic proton and Cl(1) (2.24(3) Å). Hydrogen bonds have been observed in a number of other complexes containing mutually *cis* aminophosphine and chloride ligands, and in these previous examples the H ⋯ Cl distances range from 2.1 to 2.5 Å [18a,29].

Table 2
Selected bond lengths (Å) and angles (°) for *cis*-$[PdCl_2P_2]$ (**1**)

| | | | |
|---|---|---|---|
| Pd–P(1) | 2.2535(17) | P(2)–N(1) | 1.636(4) |
| Pd–P(2) | 2.2605(14) | P(2)–N(2) | 1.676(5) |
| Pd–Cl(1) | 2.3652(18) | N(1)–C(1) | 1.492(6) |
| Pd–Cl(2) | 2.3745(16) | N(2)–C(9) | 1.501(8) |
| P(1)–N(3) | 1.637(5) | P(1)–N(4) | 1.682(9) |
| N(3)–C(23) | 1.414(8) | N(4)–C(31) | 1.484(9) |
| P(1)–Pd–P(2) | 92.42(5) | P(1)–Pd–Cl(1) | 91.13(6) |
| Cl(1)–Pd–Cl(2) | 87.42(7) | P(2)–Pd–Cl(2) | 89.04(6) |
| P(1)–N(3)–C(23) | 129.1(4) | P(1)–N(4)–C(31) | 125.0(6) |
| P(2)–N(2)–C(9) | 120.7(4) | P(2)–N(1)–C(1) | 126.3(3) |

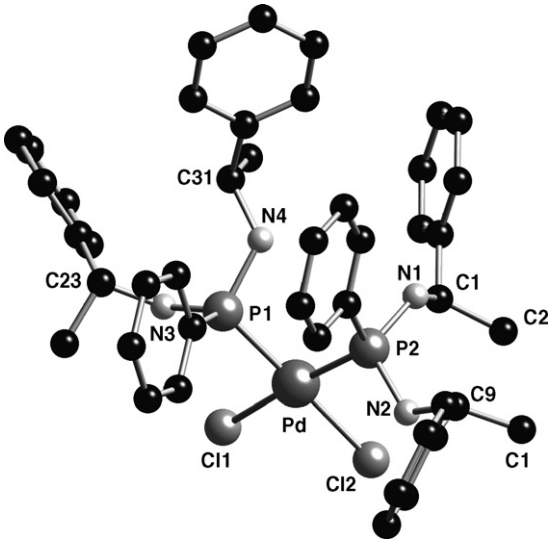


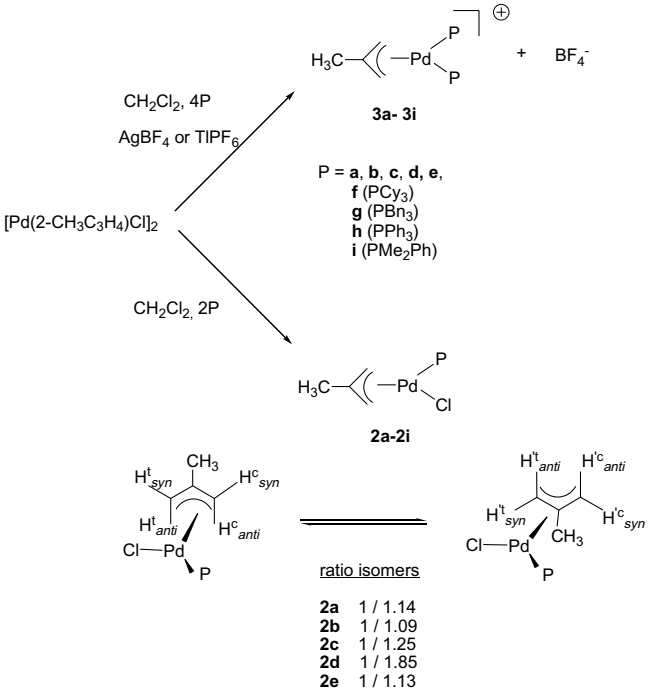

Fig. 1. Molecular structure of complex **1**.

### 2.2.2. Neutral allyl complexes $[PdCl(\eta^3\text{-}2\text{-}CH_3C_3H_4)P]$ (**2**)

Neutral allyl complexes $[PdCl(\eta^3\text{-}2\text{-}CH_3C_3H_4)P]$ (**2a**–**2e**) were prepared by reaction at low temperature of the well-known bridged chloride complex $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(\mu\text{-}Cl)]_2$ with the appropriate ligand as reported in the literature for similar compounds [12,30,31] (Scheme 2).

Complexes **2** are stable in the solid state and were fully characterized by the usual techniques. Table 3 collect NMR data for those complexes.

$^{31}P$ NMR spectra for allyl complexes showed two sharp signals arising from the two isomers formed due to the presence of a stereogenic carbon atom on the amino group. The ratio of isomers, depicted in Scheme 2, depends on the substituents in the stereogenic carbon atom of the amino groups. Naphthyl substituent in the monoaminophosphine and the phenyl substituent in bisaminophosphine lead to some discrimination between the two isomers. The phosphorus chemical shifts of complexes containing monoaminophosphino ligand (**2a**, **2b** and **2c**) lie downfield




Scheme 2.

Table 3
Selected NMR data[a] ($\delta$ ppm, in $CDCl_3$, 298 K) for neutral complexes (**2a**–**2i**) and ionic complex (**4f**)

| Complex | $\delta^{31}P$ | $\delta^1H$ ($H^t$*syn*) | $\delta^1H$ ($H^t$*anti*) | $\delta^1H$ ($H^c$*syn*) | $\delta^1H$ ($H^c$*anti*) | $\delta^1H$ ($CH_3$)[b] | $\delta^1H$ (N*H*) | $\delta^1H$ (C*H*) | $\delta^1H$ (Me)[c] |
|---|---|---|---|---|---|---|---|---|---|
| **2a** | | | | | | | | | |
| Minor | 54.6 (s) | 4.48 (bs) | 3.42 (d; 10.4) | 3.02 (bs) | 2.37 (s) | 1.84 (s) | 4.59 (dd; 19.2,2.4) | 4.05 (m) | 1.18 (d; 6.8) |
| Major | 55.1 (s) | 4.48 (bs) | 3.42 (d; 10.4) | 3.02 (bs) | 2.41 (s) | 1.84 (s) | 4.64 (dd; 19.2,4.4) | 4.05 (m) | 1.32 (d; 6.8) |
| **2b** | | | | | | | | | |
| Minor | 53.63 (s)[d] | 4.37 (m) | 3.33 (d; 4) | 2.93 (bs) | 2.34 (s) | 1.81 (s) | 4.03 (m) | 2.73 (m) | 0.85 (d; 6.8) |
| Major | 53.35 (s)[d] | 4.37 (m) | 3.30 (d; 4) | 2.85 (bs) | 2.25 (s) | 1.71 (s) | 4.03 (m) | 2.73 (m) | 0.71 (d; 6.8) |
| **2c** | | | | | | | | | |
| Minor | 53.9 (s) | 4.4 (m) | 3.37 (d; 10) | 2.92 (bs) | 2.27 (s) | 1.75 (s) | 4.83 (m) | 4.83 (m) | 1.29 (d; 6.4) |
| Major | 54.8 (s) | 4.4 (m) | 3.39 (d; 10) | 2.99 (bs) | 2.41 (s) | 1.82 (s) | 4.83 (m) | 4.83 (m) | 1.43 (d; 6.4) |
| **2d** | | | | | | | | | |
| Minor | 64.1 (s) | 4.34–4.24 | 3.25 (d; 11.2) | 2.65 (s) | 2.12 (s) | 1.6–1.5 | 3.7 (bd; 6.8)<br>4.3 (m) | 4.52–4.4<br>4.20–4.15 | 1.6–1.5 |
| Major | 63.3 (s) | 4.17 (dd; 7.6, 2.24) | 2.83 (d; 11) | 2.34 (s) | 1.40 (s) | 1.6–1.5 | 4.34–4.24<br>3.52–3.42 | 4.76–4.64<br>4.14–4.06 | 1.6–1.5 |
| **2e** | | | | | | | | | |
| Isomer I | 62.7 (s) | 4.35–4.20 | 3.34 (d; 6.8) | 2.75 (s) | 2.17 (s) | 0.9–1.4 | 3.78 (bt; 10.8)<br>3.02 (d; 10) | 3.0–2.9<br>3.3–3.42 | 0.9–1.4 |
| Isomer II | 63 (s) | 4.35–4.28 | 3.31 (d; 7.2) | 2.64 (s) | 2.33 (s) | 0.9–1.4 | 3.62 (bt; 10)<br>2.87 (d; 2.4) | 3.2–3.3<br>3.0–2.9 | 0.9–1.4 |
| **2f** | 41.2 (s) | 4.39 (m) | 3.45 (d; 8.8) | 3.15 (bs) | 2.51 (s) | 1.94 (s) | – | – | – |
| **2g** | 21.6 (s) | 4.41 (s) | 3.28 (m) | 2.55 (s) | 1.68 (s) | 1.61 (s) | – | – | – |
| **2h** | 22.4 (s) | 4.53 (bs) | 3.59 (bs) | 2.86 (s) | 2.74 (s) | 1.97 (s) | – | – | – |
| **2i** | −3.9 (s) | 4.32 (d; 6.7) | 3.35 (d; 10.2) | 3.05 (s) | 2.48 (s) | 1.83 (s) | – | – | – |
| **4f** | 42.5 (s) | 4.95 (m) | 3.66 (d; 8.4) | 3.26 (bs) | 2.61 (bs) | 1.99 (s) | | | 2.47 (s)[e] |

[a] Multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad signal. Coupling constant are given in Hz and are shown in parentheses after the multiplicity. $^1H$ NMR: 400 Hz. $^{31}P$–{$^1H$} NMR: 100.56 Hz. See Scheme 2 for atom labels.
[b] Allylic methyl group.
[c] Aminic methyl group.
[d] 273 K.
[e] Acetonitrile methyl group.

compared to that of the free ligands, but complexes containing bisaminophosphine (**2d**, **2e**) ligands show similar chemical shifts to that in free ligand. $^1H$ NMR spectra of these compounds showed two sets of signals for each *syn* and *anti* protons confirming the presence of two isomers. Proton resonances of the allylic group were assigned by comparison with literature values [12,31,32]. Monoaminophosphine complexes (**2a**–**2c**) show two sets of signals for the aminic proton but bisaminophosphine complexes (**2d**, **2e**) show two pairs of signals because of the presence of the two chiral aminophosphine substituent in each isomer. When the isomeric ratio of palladium (II) diastereoisomers is nearly 1/1 (**2e**) the $^1H$ NMR signals cannot be associated with those of $^{31}P$ NMR since the $^{31}P$–$^{13}C$ or $^{31}P$–$^1H$ correlations have not been carried out. To elucidate the solution structure of these complexes and their dynamic behaviour, 2D NOESY experiments were carried out for complexes **2a** and **2e**. NOE contacts between allylic protons and the aminophosphine ligands were not detected but interesting exchange signals between allylic protons were observed. Exchange between *syn*/*anti* allyl protons was observed selectively with the pair in *cis* to the phosphorus atom. The pair that is in *trans* position exchange only between *syn*/*syn* and *anti*/*anti* protons, in accordance with a selective opening of the palladium carbon bond *trans* to the phosphorus atom. This has been observed in analogous compounds [12,32] and suggests the well known $\eta^3$–$\eta^1$–$\eta^3$ isomerization process. Also cross-peaks that could be assigned to the whole apparent allyl rotation were observed. Exchange signals between hydrogens of the amino group of different isomers in **2e** complex are also detected as expected.

Neutral allylic complexes [PdCl($\eta^3$-2-$CH_3C_3H_4$)P] with monodentate tertiary phosphines (P = $PCy_3$ (**2f**), $PBn_3$ (**2g**), $PPh_3$ (**2h**), $PPhMe_2$ (**2i**)) were prepared by the same procedure reported in the literature [12,30,31,33] as shown in Scheme 2. Complexes **2f** and **2g** are described, to the best of our knowledge, for the first time. $^{31}P$ and $^1H$ NMR signals are reported in Table 3.

### 2.2.3. Cationic allyl complexes [Pd($\eta^3$-2-$CH_3C_3H_4$)$P_2$]$BF_4$ (**3**)

Ionic allylic complexes [Pd($\eta^3$-2-$CH_3C_3H_4$)$P_2$]$BF_4$ (**3a**–**3e**) were obtained by reaction of the dinuclear [Pd($\eta^3$-2-$CH_3C_3H_4$)($\mu$-Cl)]$_2$ with 2 equiv. of the appropriate aminophosphine ligand and subsequent treatment with $AgBF_4$ to remove the chloride ligand (Scheme 2). By the same procedure, complexes (**3f**–**3i**) were prepared

(P = $PCy_3$ (**3f**), $PBn_3$ (**3g**), $PPh_3$ (**3h**), $PPhMe_2$ (**3i**)), some of them previously reported in the literature [34]. For **3a**, **3f**, **3g** and **3i** complexes the best yields were obtained when reaction was done at 273K and for **3e** compound satisfactory elemental analysis was found using $TlPF_6$ salt instead of $AgBF_4$. The products were stable solids, fully characterized in the solid state and in solution by $^1H$ and $^{31}P$ NMR spectroscopy as shown in Table 4.

Complexes with nonchiral phosphines presented only one signal in the $^{31}P$ spectra and one broad signal for each pair of *syn* and *anti* allylic protons in the $^1H$ NMR spectra. $^{31}P$ NMR spectra of complexes with aminophosphines show two doublets of an AB spin system with coupling constants similar to those reported for similar complexes [35]. The two chiral phosphine ligands in *cis* position are formally a $C_2$ system but they loose the symmetry in the presence of the allylic group causing the two phosphorus atoms to be non-equivalent. $^1H$ NMR spectra show four different signals for the *anti* and *syn* allylic hydrogens and a unique methyl allyl signal reflecting the existence of only one isomer. 2D NOESY NMR experiment for [Pd($\eta^3$-2-$CH_3C_3H_4$)($Ph_2PNHCHCH_3Ph$)$_2$]$BF_4$ (**3a**) only showed intraligand contacts.

In the preparation of [Pd(2-$CH_3C_3H_4$)($PCy_3$)$_2$]$BF_4$ (**3f**) complex, another compound was detected. $^1H$ NMR spectroscopy indicates the presence of $\eta^1$-allyltricyclohexylphosphonium salt as confirmed by direct comparison with an authentic sample obtained by reaction of $PCy_3$ and 2-methylallylchloride [36]. The best yields in the synthesis of compound **3f** are achieved starting from [Pd($\eta^3$-2-methylallyl)($NCCH_3$)($PCy_3$)]$BF_4$ as reported by Brookhart [33].

### 2.2.4. Cationic mixed complexes [Pd($\eta^3$-2-$CH_3C_3H_4$)($NCCH_3$)P]$BF_4$ (**4**)

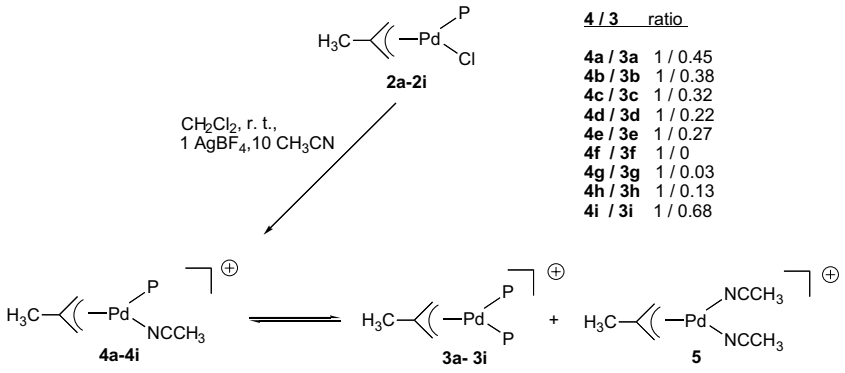
Cationic complexes [Pd($\eta^3$-2-$CH_3C_3H_4$)($NCCH_3$)P]$BF_4$ were prepared by removing the chloride by $AgBF_4$ from neutral complexes **2** in the presence of acetonitrile ligand. The reaction was followed by $^{31}P$ NMR spectroscopy showing more signals than expected, except for **4f** complex. This suggests that [Pd($\eta^3$-2-$CH_3C_3H_4$)($NCCH_3$)P]$BF_4$ (**4a**–**4e**, **4g**–**4i**) compounds undergo symmetrization, and give a mixture of the expected mixed complex **4**, the bis(acetonitrile) complex [Pd($\eta^3$-2-methylallyl)($NCCH_3$)$_2$]$BF_4$ (**5**) [37] and the symmetrical bis(phosphine) complex **3** (Scheme 3). [Pd($\eta^3$-2-$CH_3C_3H_4$)($NCCH_3$)($PCy_3$)]$BF_4$ (**4f**) complex was isolated and fully characterized in solid state. Characterization data for that compound are coincident with those reported in the literature for an analogous cation stabilized by an ether ligand [33].

Table 5 shows $^{31}P$ NMR data of the mixed cationic complexes **4a**–**4i** solutions. Complexes with aminophosphine ligands showed two doublets with chemical shift coincident with the respective symmetric cationic complexes **3a**–**3e**. For **4a**, **4c** and **4d** complexes two broad signals of different intensity also appeared suggesting the presence of the two possible isomers of the mixed cationic complexes [Pd($\eta^3$-2-$CH_3C_3H_4$)($NCCH_3$)P]$BF_4$. The ratio between the different isomers was calculated from integration signals of $^{31}P$ NMR spectra and was always nearly 1:1 except for **4d**. The same discrimination was detected for the neutral complex **2d**. For complexes **4b** and **4e** only one broad signal that can be assigned to the mixed complex appeared, probably because the chemical shift of the isomers are not different enough to be detected separately.

Table 4
Selected NMR data[a] ($\delta$ ppm, in $CDCl_3$, 298 K) for ionic complexes (**3a**–**3i**)

| Complex | $\delta^{31}P$ | $\delta^1H$ (H*syn*) | $\delta^1H$ (H*anti*) | $\delta^1H$ ($CH_3$)[b] | $\delta^1H$ (N*H*) | $\delta^1H$ (C*H*) | $\delta^1H$ (Me)[c] |
|---|---|---|---|---|---|---|---|
| **3a** | 57.3 (d; 47)<br>58.4 (d; 47) | 3.62 (bs)<br>3.68 (bs) | 3.23 (t; 9) | 1.51 (s) | 4.09 (dd; 18,10)<br>4.20 (dd; 18, 10) | 3.79 (m)<br>3.87 (m) | 0.95 (d; 7)<br>1.03 (d;7) |
| **3b** | 56.8 (s) | 3.63 (s)<br>3.69 (s) | 3.24 (bs)<br>3.27 (bs) | 1.55 (s) | 2.93 (m)<br>3.00 (m) | 2.72 (bs) | 0.66 (d; 6.5)<br>0.75 (d; 6.5) |
| **3c** | 57.7 (d; 47)<br>58.3 (d; 47) | 3.65 (bs)<br>3.67 (bs) | 3.26 (d; 8) | 1.46 (s) | 4.70 (m) | 4.53 (m) | 0.95(d; 6.4)<br>1.08 (d; 6.4) |
| **3d** | 69.2 (d; 58)<br>68.1 (d; 58) | 3.54 (t; 3.5)<br>3.66 (t; 3.5) | 2.52 (d; 11.2)<br>2.87 (d; 11.2) | 2.27 (s) | 3.06 (dd; 8.8, 4.2)<br>3.14 (t; 9.2)<br>3.70–3.76 | 3.70–3.76<br>3.86–3.97 | 1.11 (d; 6.8)<br>1.20 (d; 6.8)<br>1.25 (d; 6.8)<br>1.41 (d; 6.8) |
| **3e** | 65.8 (d; 68.8)<br>66.4 (d; 68.8) | 3.86 (s)<br>3.77 (s) | 3.0 (d; 5.6)<br>3.3 (d; 6.0) | 1.6 (s) | 3.2–2.6 | 3.2–2.6 | 0.86 (d; 6.4)<br>0.98 (d; 6.8)<br>1.02 (d; 6.4)<br>1.12 (d; 6.8) |
| **3f** | 36.0 (s) | 4.32 (bs) | 3.08 (bs) | 0.95–2.06 | – | – | – |
| **3g** | 9.7 (s) | 3.62 (s) | 2.16 (s) | 0.98 (s) | – | – | – |
| **3h** | 23.1 (s) | 3.72 (bs) | 3.62 (s) | 1.87 (s) | – | – | – |
| **3i** | −8.4 (s) | 4.06 (s) | 3.20 (bs) | 1.82 (s) | – | – | – |

[a] Multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad signal. Coupling constant are given in Hz and are shown in parentheses after the multiplicity. $^1H$ NMR: 400 Hz. $^{31}P$–{$^1H$} NMR: 100.56 Hz.
[b] Allylic methyl group.
[c] Aminic methyl group.




Scheme 3.

Table 5
Selected $^{31}P$ NMR data[a] ($\delta$ ppm, 298 K) for $CH_2Cl_2$ solution of complexes $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(NCCH_3)(P)]BF_4$ (**4a–4i**)

| P | $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(NCCH_3)(P)]^{+}$[b] | $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(P)_2]^{+}$ |
|---|---|---|
| **a** | 52.6 (bs) [1.2] | 57.4 (d; 47) |
| | 57.0 (bs) [1.0] | 58.6 (d; 47) |
| **b** | 57.3 (bs) | 58.3 (s) |
| **c** | 56.2 (bs) [1.0] | 57.9 (d; 47) |
| | 57.0 (bs) [1.0] | 58.5 (d; 47) |
| **d** | 65.9 (bs) [1.5] | 69.2 (d; 58) |
| | 67.9 (bs) [1.0] | 68.1 (d; 58) |
| **e** | 67.1 (bs) | 65.8 (d; 68.8) |
| | | 66.4 (d; 68.8) |
| **f** | 42.5 (s) | – |
| **g** | 19.8 (bs) | 9.7 (s) |
| **h** | 24.9 (bs) | 23.3 (s) |
| **i** | −4.5 (bs) | −8.4 (s) |

[a] Multiplicity: s, singlet; d, doublet; b, broad signal. Coupling constant are given in Hz and are shown in parentheses after the multiplicity. $^{31}P\text{-}\{^1H\}$ NMR: 100.56 Hz.
[b] Isomer ratio is shown in brackets.

Presumably broad signals are due to the lability of the acetonitrile ligand. Solutions of complexes **4g–4i** showed two broad signals, one of them coincident with the respective symmetrical complex and the other assigned to the mixed acetonitrile cationic complex **4g–4i**. Solutions of complex **4f** only showed one signal corresponding to the mixed complex and no signals of the products coming from the symmetrization reaction were observed.

### 2.3. Study of the symmetrization reaction of complexes $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(NCCH_3)P]BF_4$ (4)

Solutions of cationic mixed complexes type **4** obtained '*in situ*', are used as catalytic precursors in several reactions, so the study of the symmetrization equilibrium is important to evaluate the consequences in the catalytic processes. The reaction was studied with the chiral phosphines **a**, **b**, **c**, **d** and **e**, and also with nonchiral phosphines **f**, **g**, **h** and **i** in order to relate the steric and/or electronic effects of phosphine ligand with the extension of the symmetrization process.

A solution of complexes **4a–4i** in $CH_2Cl_2$ was reacted with the stoichiometric amount of $AgBF_4$ in the presence of a ten fold excess of acetonitrile. According to the results of the $^{31}P$ NMR spectra, the crude mixtures contained the mixed (phosphine/acetonitrile) ionic complex (**4**) and the bis(phosphine)ionic complex (**3**) in a relation shown in Scheme 3, the bisacetonitrile complex **5** must be also present. The results show few variation of the symmetrization reaction within complexes (**4a–4c**) and bisaminophosphine complexes (**4d**, **4e**). The different extension of the symmetrization reaction observed for mixed cationic complexes with monodentate tertiary phosphines seems to be related to the steric over the electronic parameter [26]. The compound containing the phosphine with the highest value of the cone angle ($PCy_3$) does not suffer the symmetrization reaction and, in fact, is the only case where the cationic mixed complex $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(NCCH_3)(PCy_3)]BF_4$ was fully characterized in the solid state (selected NMR data are shown in Table 3). The same observation can be described for complexes **4a–4e**, those containing monoaminophosphines show a greater tendency to the symmetrization than those with bisaminophosphines. Moreover, reaction of the stoichiometric amount of **4c** and **5** complexes in $CH_2Cl_2$ leads to an equilibrium mixture of **3c**, **4c** and **5**. Symmetrization reaction has been reported in the literature [31] for complexes $[Pd(\eta^3\text{-allyl})L^1L^2]^+$ ($L^1 = PPh_3$, $L^2 = NCCH_3$, py). The synthesis and characterization of the mixed complex $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(NCCH_3)(PBnCyPh)]BF_4$ reported in the literature [11a] agrees with the statement that symmetrization reaction is nearly unobservable with bulky phosphines.

## 3. Hydrovinylation reaction

The solution of mixed allylic cationic complexes (**4a–4h**) were tested as catalytic precursors in the hydrovinylation reaction of styrene with ethylene and the results are shown in Table 6.

The hydrovinylation reaction was always carried out using a [Pd]/styrene ratio of 1/1000, $CH_2Cl_2$ as solvent, 15 bar of pressure and at 25 °C temperature. The products of the catalytic process were analyzed after 60 or 360 min

Table 6
Hydrovinylation of styrene[a]

| Entry | Phosphine | Time (min) | Conversion[b] (%) | Codimer[c] (%**A** + **B** + **C**) | Selectivity[d] (%**A**) | TOF[e] (total Pd) | TOF[f](active Pd) |
|---|---|---|---|---|---|---|---|
| 1 | **a**[g] | 60 | 1.6 | 1.6 | 99.8 | 16 | 23 |
| 2 | **a**[h] | 60 | 10.4 | 9.7 | 97.8 | 104 | |
| 3 | **a**[h] | 360 | 76.4 | 74.1 | 69.5 | 127 | |
| 4 | **b**[g] | 60 | 1.6 | 74.1 | 99.5 | 16 | 22 |
| 5 | **b**[h] | 60 | 22.6 | 20.9 | 93.9 | 226 | |
| 6 | **b**[h] | 360 | 97.3 | 93.1 | 34.7 | 162 | |
| 7 | **c**[g] | 60 | 3.2 | 0.7 | 99.6 | 32 | 43 |
| 8 | **c**[h] | 60 | 8.6 | 8.2 | 98.8 | 86 | |
| 9 | **c**[h] | 360 | 72.7 | 71.0 | 72.9 | 121 | |
| 10 | **d**[h] | 60 | 7.8 | 6.6 | 98.4 | 78 | |
| 11 | **d**[h] | 360 | 29.3 | 25.9 | 82.5 | 49 | |
| 12 | **e**[h] | 60 | 5.5 | 4.5 | 99.3 | 55 | |
| 13 | **e**[h] | 360 | 20.1 | 17.8 | 95.2 | 33 | |
| 14 | **f**[i] | 60 | 14.3 | 12.6 | 99.6 | 143 | 143 |
| 15 | **g**[g] | 60 | 62.4 | 61.5 | 94.2 | 624 | 643 |
| 16 | **g**[h] | 60 | 77.7 | 75.9 | 89.8 | 777 | |
| 17 | **h**[g] | 60 | 22.2 | 21.8 | 96.4 | 222 | 252 |
| 18 | **styrene**[j] | 60 | 1.9 | 1.9 | 86.1 | 19 | |
| 19 | **styrene**[j] | 120 | 5.5 | 5.5 | 78.5 | 28 | |
| 20 | **styrene**[j] | 240 | 14.4 | 14.4 | 60.0 | 36 | |

[a] Reaction carried out at 25 °C, and 15 bar of initial pressure of ethylene in 10 mL of $CH_2Cl_2$; ratio styrene/Pd 1000/1.
[b] Conversion of starting styrene.
[c] Codimer: total amount of codimers: see Eq. (1).
[d] Selectivity: % of 3-phenyl-1-butene with respect to the codimers.
[e] TOF = (mol codimer) (mol neutral complex)$^{-1}$ (h)$^{-1}$.
[f] TOF = (mol codimer) (mol cationic mixed complex)$^{-1}$ (h)$^{-1}$.
[g] Precursor obtained by reaction of **2** with $AgBF_4$ and $CH_3CN$ (method A).
[h] Precursor obtained by reaction of **2** with $AgBF_4$ (method B).
[i] $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(NCCH_3)(PCy_3)]BF_4$.
[j] Precursor obtained by reaction of 1 equiv. $[PdCl(\eta^3\text{-}2\text{-}CH_3C_3H_4)]_2$ with 2 equiv. of $AgBF_4$.

reaction. Actually, only in the case of **4f** complex was possible to introduce a well-defined precursor (entry 14). After 1 h reaction low conversion (12% codimers) but good selectivity (99 % of 3-phenyl-1-butene) was found. As described above, mixed allylic cationic complexes (**4a**–**4e**, **4g** and **4h**) undergo symmetrization in some degree, leading to solutions were symmetric bisphosphine complexes type **3**, mixed complexes type **4** and $[Pd(\eta^3\text{-}2\text{-methylallyl})(NCCH_3)_2]BF_4$ (**5**) complex are in equilibrium. To analyze the results from the hydrovinylation reaction under comparable experimental conditions to those used in the study of the symmetrization equilibrium, we prepared the solutions of the precursors by reaction of the stoichiometric amounts of the neutral complex (**2a**–**2e**, **2g** and **2h**) and $AgBF_4$ in $Cl_2CH_2$ to which a 10-fold excess of acetonitrile was added and the AgCl filtered off. The activity of complexes **3** and **5** was studied. All the cationic complexes $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)P_2]BF_4$ (**3a**–**3i**) were tested under the same catalytic conditions showing no conversion and recovered unaltered. Although the literature states that $[PdR(NCCH_3)P_2]BF_4$ complexes are readily activated in the presence of ethylene, it seems that ethylene is not able to perform by itself the substitution of certain phosphines or induce the $\eta^3$–$\eta^1$ shift on the allyl moiety [12]. Complex $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(NCCH_3)_2]BF_4$ (**5**) did not present any catalytic activity for hydrovinylation under the experimental conditions. The same result was reported in the literature [38] for olefin isomerization and oligomerization reaction. In consequence, when solutions of the mixed cationic compounds **4** were used as catalytic precursors, only $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(NCCH_3)P]BF_4$ complexes were able to generate the active species. Moreover, $^{31}P$ NMR spectra of the solutions after one or 3 h of reaction showed the presence of the symmetrical bisphosphine complexes $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)P_2]BF_4$ (**3**) suggesting that the equilibrium was not shifted towards the formation of active mixed complex in the reaction conditions. Therefore, in order to properly compare the activity of the different precursors it is necessary to use TOF values calculated from the amount of the mixed complex in the equilibrium and not from the amount of the starting neutral complex used in the preparation of the precursor solution. Both TOF values are depicted in Table 6 when data are available.

The best catalytic properties for the formation of 3-phenyl-1-butene is observed with the mixed complex $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(NCCH_3)PBn_3]BF_4$ (**4g**) (entries 15 vs. 1, 4, 7, 14, 17). This fact suggests that the steric bulk and electronic properties in $PBn_3$ ligand allow a good stabilization of hydride active species and a fast reaction, as described for nickel complexes [39]. The data also reflect that substitution of one or two P–C bonds by P–N bonds in phosphine ligands cause a great decrease in the activity of the precursor (entries 17 vs 2, 5, 8, 10, 12). It seems that these aminophosphine ligands are less suitable to stabilize the

proposed hydride species in contrast with some results reported in the literature for nickel complexes with chiral phosphoramidite ligands [8].

It is known that the presence of acetonitrile in the reaction medium can compete with styrene and ethylene by the open coordination position. This kind of competence alters the precursor activity, so we prepared mixed cationic compounds in the absence of acetonitrile and we analyzed the species existing in these solutions. To a dichlorometane solution of the neutral complex [Pd($\eta^3$-2-$CH_3C_3H_4$)-(Cl)($Ph_2PNHCHCH_3Naph$)] (**2c**), the stoichiometric amount of $AgBF_4$ was added in the presence of 1000-fold styrene excess. The AgCl was filtered off and the solution monitored by $^{31}P$ NMR spectroscopy. A quantitative analysis of the species in equilibrium was not possible because very broad signals appeared probably due to their lability. The spectrum showed two broad doublets at 57.6 ppm and 56.8 ppm ($J = 47$ Hz), assigned to the [Pd($\eta^3$-2-$CH_3C_3H_4$)$P_2$]$BF_4$ (**3c**) complex and a very broad signal at 58.2 ppm tentatively assigned to the mixed species [Pd($\eta^3$-2-$CH_3C_3H_4$)(styrene)($Ph_2PNHCHCH_3Naph$)]$BF_4$. Consequently, [Pd($\eta^3$-2-$CH_3C_3H_4$)(styrene)$_2$]$BF_4$ complex must be also present in the solution although it is not detected. We prepared the symmetrical bisstyrene palladium(II) complex by reaction of the dinuclear [Pd($\eta^3$-2-$CH_3C_3H_4$)Cl]$_2$ with $AgBF_4$ in the presence of styrene and the filtered solution was introduced in the reactor in the catalytic conditions. Table 6 shows that [Pd($\eta^3$-2-$CH_3C_3H_4$)(styrene)$_2$]$BF_4$ is moderately active (entries 18, 19, 20), showing high selectivity to 3-phenyl-1-butene at low conversions but a considerable amount of styrene dimerization (1,3-diphenyl-1-butene) is obtained. Isomerization compounds (**B**, **C**) were obtained at higher conversions (entries 18, 19, 20).

Precursors obtained in the absence of acetonitrile leads to higher conversions and lower selectivites (entries 1, 4, 7, 15 vs. 2, 5, 8, 16). The same result is obtained when reaction time is increased to 6 h (entries 2, 5, 8, 10, 12 vs. 3, 6, 9, 11, 13). This fact indicates that 3-phenyl-1-butene formed in the reaction may coordinate to the palladium centre without the competence of $CH_3CN$. Consequently 3-phenyl-1-butene so formed isomerizes to 2-phenyl-2-butene. Moreover the presence of [Pd($\eta^3$-2-$CH_3C_3H_4$)(styrene)$_2$]$BF_4$ complex also increases the formation of the isomerization products. When reaction time changes from 1 to 6 h TOF values (calculated with total amount of Pd(II) introduced) increase for complexes with aminophosphine ligand **a** and **c** (entries 2, 3, 8 and 9), while decrease for **d** and **e** (entries 10, 11, 12 and 13) suggesting that monoaminophosphine ligands stabilize better the active hydride species than does bisaminophosphine. The increase in the TOF values for **a** and **c** ligands can be argued taking account of the existence of an initial activation time for the precursor. For ligand **b** only a small decrease of TOF is observed, probably because after 6 h of reaction styrene was exhausted (entries 5 and 6).

Disappointing values of enantioselectivity were obtained with precursors containing chiral monoamino and bisaminophosphine ligands (only for **b** ligand a 11% ee was obtained, (*S*)-3-phenyl-1-butene isomer [11b]) showing that the chirality over the carbon backbone of the amino group has hardly any discriminating effect.

## 4. Conclusions

The susceptibiliy of aminophosphines and bis(aminophosphine) ligands to air, moisture and protic solvents was not a limitation for the preparation of stable allylic neutral and cationic palladium complexes [Pd($\eta^3$-2-methylallyl)ClP] and [Pd($\eta^3$-2-methylallyl)$P_2$]$BF_4$. The results described here in relation to the symmetrization equilibrium experienced by cationic complexes [Pd($\eta^3$-2-methylallyl)($NCCH_3$)P]$BF_4$ may be considered as a warning in the study of a catalytic reaction where the catalyst is prepared in situ. Such a procedure is correct and may provide reliable results only when the quantitative formation of the catalytically active precursor is proved to occur within the residence time preceding the addition of the other reagents involved in the process. The species formed because of symmetrization of catalytic precursors are not innocent although in our case the results of the hydrovinylation reaction are not substantially modified. The presence of [Pd($\eta^3$-2-$CH_3C_3H_4$)(styrene)$_2$]$BF_4$ complex increases the amount of styrene dimerization and isomerization compounds (**B**, **C**) and contribute to a decrease of the enantioselectivity of the process at high conversions. The cationic complexes [Pd($\eta^3$-2-$CH_3C_3H_4$)$P_2$]$BF_4$ are responsible of a decrease in the conversion of the process. Although chiral monodentate aminophosphine ligands are easily prepared, those presented in the present paper show moderate activity, low enantioselectivity but good selectivity towards 3-phenyl-1-butene in the asymmetric hydrovinylation catalytic process. Probably aminophosphine (and particularly bisaminophosphine) ligands do not stabilize the hydride active species and, furthermore, the chiral centre is too far from the metal to induce good enantiodiscrimination.

## 5. Experimental

### 5.1. General methods

All compounds were prepared under a purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen. (*R*)-α-methylbenzylamine, (*R*)-1-(1-Naphthyl)ethylamine and (*R*)-1-cyclohexylethylamine (Aldrich) and $PPh_3$, $PMe_2Ph$, $PCy_3$ (Strem) were used as supplied. $PBn_3$ [40], [Pd($\eta^3$-2-$CH_3C_3H_4$)(μ-Cl)]$_2$ [41], [PdCl($\eta^3$-2-$CH_3C_3H_4$)($PPh_3$)] [31], [PdCl($\eta^3$-2-$CH_3C_3H_4$)($PMe_2Ph$)] [30], [Pd($\eta^3$-2-$CH_3C_3H_4$)($PPh_3$)$_2$]$BF_4$ [34] and [Pd($\eta^3$-2-$CH_3C_3H_4$)($NCCH_3$)$_2$]$BF_4$ [31] were prepared as previously described. The $^1H$, $^{13}C$, and $^{31}P$

NMR spectra were recorded on either a Varian XL-500 and Mercury-400 MHz ($^1$H, standard $SiMe_4$), Varian Gemini ($^{13}$C, 50 MHz, standard $SiMe_4$) and Bruker DRX 250 ($^{31}$P, 101 MHz, standard $H_3PO_4$) spectrometers in $CDCl_3$ unless otherwise cited. Chemical shifts in ppm were reported downfield from standards. The two-dimensional experiments were carried out with a Bruker DMX500 or a Varian XL-500 instruments, at 298 K with mixing time of 500 ms. IR spectra were recorded on the following spectrometers: FT-IR Nicolet 520, FT-IR Nicolet Impact 400, FT-IR Avatar 330 and FTIR Nicolet 5700. FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument. The routine GC analyses were performed on a Hewlett–Packard 5890 Series II gas chromatograph (50-m Ultra 2 capillary column 5% phenylmethylsilicone and 95% dimethylsilicone) with a FID detector. Enantiomeric excess was determined by GC on a Hewlett–Packard 5890 Series II gas chromatograph (30-m Chiraldex DM column) with a FID detector. Elemental analyses were carried out by the Serveis Cientificotècnics of the Universitat Rovira i Virgili in an Eager 1108 microanalyzer. Optical rotations were measured on a Perkin Elmer 241MC spectropolarimeter at 23 °C.

### 5.2. Synthesis of phosphines

#### 5.2.1. Synthesis of diphenyl [(*R*)-(1)-phenylethylamino]-phosphine (**a**)

Following the same method described in the literature for $Ph_2PNH$(*S*)-$CHCH_3Ph$ [24]. (*R*)-α-methylbenzylamine (1.30 ml, 10 mmol) and $NEt_3$ (2.10 ml, 15 mmol) were dissolved in 15 mL of toluene and the solution was cooled to 0 °C. A solution of $PPh_2Cl$ (1.80 mL, 10 mmol) in toluene (15 mL) was added dropwise. The mixture was then stirred for 1.5 h at room temperature and the colourless precipitate of triethylamine hydrochloride was filtered off. The solvent and excess of triethylamine were removed in vacuum. A colourless oil was obtained and used without purification. Yield: 80%. $^1$H NMR ($CDCl_3$, 200 MHz): [δ/ppm] 1.39 (d, $J_{HH} = 7.0$, 3H), 2.18 (bs, 1H), 4.22 (m, 1H), 7.19–7.85 (m, 15H). $^{13}$C NMR ($CDCl_3$, 50 MHz): [δ/ppm] 24.82 (d, $J_{CP} = 7.3$, $CH_3$), 55.36 (d, $J_{CP} = 22.7$, CH), 124.79–131.37 (Ar). $^{31}$P NMR (toluene, 101 MHz): [δ/ppm] 36.0. MS-CI (NBA, *m*/*z*): 305 $[M]^+$. $[\alpha]^{298}$ ($c = 0.813$, $CH_2Cl_2$) = +6.5.

#### 5.2.2. Synthesis of diphenyl [(*R*)-1-cyclohexylethylamino]-phosphine (**b**)

Prepared analogously to (**a**) from (*R*)-1-cyclohexylethylamine. The colourless oil obtained was used without purification. Yield: 84%. $^1$H NMR ($CDCl_3$, 200 MHz): [δ/ppm] 0.99 (d, $J_{HH} = 6.8$, 3H), 0.86–1.74 (m, 12H), 2.93 (m, 1H), 7.22–7.90 (10H). $^{13}$C NMR ($CDCl_3$, 50 MHz): [δ/ppm] 19.74 (d, $J_{CP} = 5.9$, $CH_3$), 25.34, 25.43, 25.66, 27.51, 28.35 (s, $CH_2$), 44.43 (d, $J_{CP} = 6.4$, CH), 57.10 (d, $J_{CP} = 24.1$, CH), 126.9–131.22 (Ar). $^{31}$ P NMR (toluene, 101 MHz): [δ/ppm] 36.4. MS-CI (NBA, *m*/*z*): 311 $[M]^+$. $[\alpha]^{298}$ ($c = 0.908$, $CH_2Cl_2$) = −18.

#### 5.2.3. Synthesis of diphenyl[1-(*R*)-(1-naphthyl)ethylamino] phosphine (**c**)

Prepared analogously to (**a**) from (*R*)-1-(1-naphthyl)ethylamine. The colorless oil obtained was used without purification. Yield: 85%. $^1$H NMR ($CDCl_3$, 200 MHz): [δ/ppm] 1.52 (d, $J_{HH} = 7$, 3H), 2.26 (bs, 1H), 5.02 (m, 1H), 7.13–8.03 (17H). $^{13}$C NMR ($CDCl_3$, 50 MHz): [δ/ppm] 24.12 (d, $J_{CP} = 6.4$, $CH_3$), 51.19 (d, $J_{CP} = 23.2$, CH), 120.83–141.37 (Ar). $^{31}$ P NMR (toluene, 101 MHz): [δ/ppm] 36.5. MS-CI (NBA, *m*/*z*): 355 $[M]^+$. $[\alpha]^{298}$ ($c = 0.858$, $CH_2Cl_2$) = −61.4.

#### 5.2.4. Synthesis of phenylbis[1-(*R*)-phenylethylamino]-phosphine (**d**)

Following a slight modification of the method described in the literature for $PhP[NH(S)\text{-}CH(CH_3)Ph]_2$ [25] (*R*)-(+)-α-methylbenzylamine (2.69 mL, 20 mmol) and $NEt_3$ (4.18 mL, 30 mmol) were dissolved in 20 mL of toluene and the solution was cooled at 0°C. A solution of $PPhCl_2$ (1.40 mL, 10 mmol) in toluene (15 mL) was added dropwise. After the addition was finished the mixture was stirred for 1.5 h at room temperature and the precipitate was filtered off. The solvent and excess of triethylamine were removed in vacuo. A colourless oil was obtained and used without purification. Yield: 80%. $^1$H NMR ($CDCl_3$, 250 MHz): [δ/ppm] 1.31 (d, $J_{HH} = 6.6$, 3H), 1.48 (d, $J_{HH} = 6.6$, 3H), 2.42 (d, $J_{HH} = 6.7$, 1H), 2.53 (t, $J_{HH}$–$J_{PH} = 7.2$, 1H), 4.18–4.02 (2H), 7.18–7.65 (15H). $^{13}$C NMR ($CDCl_3$, 50 MHz): [δ/ppm] 26.02 (d, $J_{CP} = 8.3$, $CH_3$), 26.76 (d, $J_{CP} = 3.9$, $CH_3$), 54.85 (d, $J_{CP} = 19.0$, CH), 53.53 (d, $J_{CP} = 12.2$, CH),125.83–143.68 (Ar). $^{31}$P NMR ($CDCl_3$, 101 MHz): [δ/ppm] 59.1. MS-CI (NBA, *m*/*z*): 348 $[M]^+$. $[\alpha]^{298}$ ($c = 2.67$, $CH_2Cl_2$) = +47.94.

#### 5.2.5. Synthesis of phenylbis[1-(*R*)-cyclohexylethylamino]-phosphine (**e**)

The procedure used was the same as for (**d**) starting from the amine (*R*)-1-cyclohexylethylamine. A viscous oil was obtained and used as such for the next step. Yield: 75%. $^1$H NMR ($CDCl_3$, 250 MHz): [δ/ppm] 0.9–1.9 (28H), 1.92 (dd, $J_{HH} = 6.7$, 1H), 2.05 (d, $J_{HH} = 8.2$, 1H), 2.9–3.1 (2H), 7.18–7.84 (5H). $^{13}$C NMR ($CDCl_3$, 50 MHz): [δ/ppm] 20.87 (d, $J_{CP} = 6.1$, $CH_3$), 21.32 (d, $J_{CP} = 3.8$, $CH_3$), 26.46–29.95 ($CH_2$), 46.10–45.90 (CH), 55.49 (d, $J_{CP} = 18$, CH), 55.84 (d, $J_{CP} = 19$, CH), 127.84–145.69 (Ar). $^{31}$P NMR ($CDCl_3$, 101 MHz): [δ/ppm] 60.7. MS-CI (NBA, *m*/*z*): 360 $[M]^+$. $[\alpha]^{298}$ (9ic = 0.860, $CH_2Cl_2$) = −19.19.

### 5.3. Synthesis of dichlorobis[phenylbis((*R*)-1-phenylethylamino)phosphine]palladium(II) (**1**)

0.714 g (2.5 mmol) of $PdCl_2$(COD) and 1.74 g (5 mmol) of phosphine d were dissolved in 20 mL of $CH_2Cl_2$ at room temperature. After 2 h stirring, the resulting red solution was concentrated under vacuum and 10 mL of ether were added. The orange precipitate was filtered and dried. Yield: 1.0 g (49% ). $^1$H NMR (250 MHz, $CDCl_3$): [δ/ppm] 1.14 (d;

7.2, 3H), 1.37 (d; 6.8, 3H), 3.26 (dd; 9.2, 5.6, 1H) 3.5 (m, 1H), 4.6 (m, 1H), 4.8 (dd; 11.6, 9.6, 1H), 6.4–7.31 (15H). $^{31}$P (101 MHz, $CH_2Cl_2$): [$\delta$/ppm] 57,1 (s). Anal. Calc. for $C_{44}H_{50}Cl_2N_4P_2Pd$: C, 58.16; N, 6.78; H, 6.10. Found: C, 56.63; N, 5.92; H, 5.97%. MS/ESI (+): *m*/*z* 839.4 $[M-Cl]^+$.

### 5.4. Synthesis of complexes [PdCl($\eta^3$-2-methylallyl)P] (2)

The complexes were obtained by similar procedures described in the literature for complexes (**2h**) [31] and (**2i**) [30].

#### 5.4.1. Chloro($\eta^3$-2-methylallyl){diphenyl[(*R*)-(1)-phenylethylamino]phosphine}palladium(II) (2a)

0.98 g (2.5 mmol) of [Pd($\eta^3$-2-methylallyl)($\mu$-Cl)]$_2$ were dissolved in 5 mL of dichloromethane and 1.53 g (5 mmol) of phosphine (**a**) dissolved in 10 mL of $CH_2Cl_2$ were added. The mixture was stirred at −20 °C for 1 h and the solvent removed under reduced pressure. Addition of ether (5 mL) lead to an orange solid. Yield: 0.51 g (20%). $^1$H NMR (400 MHz, $CDCl_3$, 298 K): [$\delta$/ppm] 1.18, 1.32 (d, $J_{HH} = 6.8$, 3H); 1.84 (s, 3H); 2.37, 2.41 (s, 1H); 3.02 (bs, 1H); 3.42 (s, $J_{PH} = 10.4$, 1H); 4.05 (m, 1H); 4.48 (bs, 1H); 4.64, 4.59 (dd, $J_{PH} = 19.2$, $J_{HH} = 4.4$, 1H); 7.00–7.74 (15H). $^{31}$P NMR (101 MHz, $CH_2Cl_2$, 298 K): [$\delta$/ppm] 54.6 (s), 55.1 (s). Anal. Calc. for $C_{24}H_{27}ClNPPd$: C, 57.39; H, 5.42; N, 2.29. Found: C, 56.74; H, 6.0; N, 2.82%.

#### 5.4.2. Chloro($\eta^3$-2-methylallyl){diphenyl[(*R*)-1-cyclohexylethylamino]phosphine}palladium(II) (2b)

Complex (**2b**) was synthesized in a similar way to that used for (**2a**). Starting materials for **2b**: 0.942 g (2.39 mmol) of palladium [Pd($\eta^3$-2-methylallyl)($\mu$-Cl)]$_2$ and 1.5 g (4.82 mmol) of phosphine (**b**). A yellow solid was obtained. Yield: 0.48 g (24%). $^1$H NMR (400 MHz, $CDCl_3$, 298 K): [$\delta$/ppm] 0.71, 0.85 (d, $J_{HH} = 6.8$, 3H); 0.73–1.61 (22H), 1.72, 1.81 (s, 3H); 2.25, 2.34 (s, 2H); 2.73 (m, 2H); 2.85, 2.93 (bs, 2H); 3.30, 3.33 (d, $J_{PH} = 4.0$, 2H); 4.03 (m, 2H); 4.37 (m, 2H); 7.32–7.69 (20H). $^{31}$P NMR (101 MHz, $CDCl_3$, 273 K): [$\delta$/ppm] 53.63 (s), 53.35 (s). Anal. Calc. for $C_{24}H_{33}ClNPPd$: C, 56.70; H, 6.54; N, 2.76. Found: C, 56.21; H, 6.99; N, 2.68%.

#### 5.4.3. Chloro($\eta^3$-2-methylallyl){diphenyl[1-(*R*)-(1-naphtyl)ethylamino]phosphine]palladium(II) (2c)

Complex (**2c**) was synthesized in a similar way to that used for preparation of (**2a**). Starting materials for (**2c**): 0.729 g (1.85 mmol) of [Pd($\eta^3$-2-methylallyl)($\mu$-Cl)]$_2$ and 1.33 g (375 mmol) of phosphine (**c**). A pale yellow solid was obtained. Yield: 1.35 g (66%). $^1$H NMR (400 MHz, $CDCl_3$, 298 K): [$\delta$/ppm] 1.29, 1.43 (d, $J_{HH} = 6.4$, 3H); 1.75, 1.82 (s, 3H); 2.27, 2.41 (s, 2H); 2.92, 2.99 (bs, 2H); 3.37, 3.39 (d, $J_{PH} = 10.0$, 2H); 4.44 (m, 2H); 4.83 (m, 4H); 6.65–7.69 (17H). $^{31}$P NMR (101 MHz, $CH_2Cl_2$, 298 K): [$\delta$/ppm] 54.8 (s), 53.9 (s). Anal. Calc. for $C_{28}H_{29}ClNPPd$: C, 60.88; H, 5.29; N, 2.54. Found: C, 60.54; H, 5.43; N, 2.57%.

#### 5.4.4. Chloro($\eta^3$-2-methyallyl){phenylbis[1-(*R*)-phenylethylamino]phosphine} palladium(II) (2d)

To [Pd($\eta^3$-2-methylallyl)($\mu$-Cl)]$_2$ (0.98 g, 2.5 mmol) in $CH_2Cl_2$ (5 mL) a solution of phenylbis(1-(*R*)-phenylethylamino)phosphine (**d**) (5 mmol) in 5 mL of $CH_2Cl_2$ was added. The mixture was stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure. Addition of 5 mL of diethylether lead to a yellow solid. Yield: 2.109 g (78%). $^1$H NMR (400 MHz, $CDCl_3$, 298 K): [$\delta$/ppm] 1.5–1.6 (9H); 1.40, 2.12 (s, 1H); 2.34, 2.65 (s, 1H); 2.83, 3.25 (d, $J_{PH} = 11$, 1H); 3.7–4.8 (5H); 7.16–7.57 (15H). $^{31}$P NMR (101 MHz, $CDCl_3$, 298 K): [$\delta$/ppm] 64.1(s), 63.3 (s). Anal. Calc. for $C_{26}H_{32}ClN_2PPd$: C, 57.26; H, 5.91; N, 5.14. Found: C, 57.82; H, 6.83; N, 5.17%. MS-FAB (NBA, *m*/*z*): 509 $[M^+]-Cl$.

#### 5.4.5. Chloro($\eta^3$-2-methyallyl){phenylbis[1-(*R*)-cyclohexylethylamino]phosphine}palladium(II) (2e)

[Pd($\eta^3$-2-methylallyl)($\mu$-Cl)]$_2$ (0.98 g, 2.5 mmol) was dissolved in 5 mL of $CH_2Cl_2$ and the solution was cooled to 0 °C. A solution of phenylbis (1-(*R*)-cyclohexylethylamino)phosphine (**e**) (5 mmol in 5 mL of $CH_2Cl_2$) was added. The mixture was stirred at 0 °C for 1 h and then warmed to room temperature. After stirring for 1 h, the solvent was evaporated under reduced pressure. On addition of ether (5 mL) a yellow powder is formed. Yield: 2.358 g (63%). $^1$H NMR (400 MHz, $CDCl_3$, 298 K): [$\delta$/ppm] 0.9–1.8 (31H); 2.17, 2.33 (s, 1H); 2.64, 2.75 (s, 1H); 2.9–3.8 (5H); 4.3–4.4 (1H); 7.4–7.7 (5H). $^{31}$P NMR (101 MHz, $CDCl_3$, 298 K): [$\delta$/ppm] 63.0(s), 62.7 (s). Anal. Calc. for $C_{26}H_{44}ClN_2PPd$: C, 55.37; H, 8.92; N, 4.71. Found: C, 56.02; H, 7.96; N, 4.71%. MS-FAB (NBA, *m*/*z*): 521 $[M]^+-Cl$.

#### 5.4.6. Chloro($\eta^3$-2-methylallyl)(tricyclohexylphosphine)-palladium(II) (2f)

Compound (**2f**) is synthesized in a similar way to that used for the preparation of (**2a**). Starting materials: 4.27 mmol of $PCy_3$ (7.56 ml of a 20% toluene solution) and 2.13 mmol (0.841 g) of [Pd($\eta^3$-2-methylallyl)($\mu$-Cl)]$_2$. The solvent was evaporated under reduced pressure and ether/hexane was added. After 2 h at 0 °C a pale yellow solid was formed. Yield: 1.134 g (56%). $^1$H NMR (200 MHz, $CDCl_3$, 298 K): [$\delta$/ppm] 1.94 (s, 3H), 1.26–2.22 (33H), 2.51 (s, 1H), 3.15 (bs, 1H), 3.45 (d, $J_{PH} = 8.8$, 1H), 4.39 (m, 1H). $^{31}$P NMR (101 MHz, $CH_2Cl_2$, 298 K): [$\delta$/ppm] 41.2 (s). Anal. Calc. for $C_{22}H_{40}ClPPd$: C, 55.35; H, 8.45. Found: C, 55.62; H, 9.42%.

#### 5.4.7. Chloro($\eta^3$-2-methylallyl)(tribenzylphosphine)-palladium(II) (2g)

The tribenzylphosphine (**g**) (0.77 g, 1.28 mmol) and [Pd($\eta^3$-2-methylallyl)($\mu$-Cl)]$_2$ (0.5. g, 2.54 mmol) were dissolved in 40 ml of dichloromethane. The solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and hexane addition

(10 mL) caused the precipitation of a white solid. Yield: 0.97 g (76%). $^1$H NMR (200 MHz, CDCl3, 298 K): [δ/ppm] 1.61 (s, 3H), 1.68 (s, 1H), 2.55 (s, 1H), 3.28 (7H), 4.41 (bs, 1H), 7.27 (m, 15H). $^{31}$P NMR (101 MHz, $CH_2Cl_2$, 298 K): [δ/ppm] 21.6 (s). Anal. Calc. for $C_{25}H_{28}ClPPd$: C, 59.90; H, 5.63. Found: C, 59.68; H, 5.61%.

### 5.5. Synthesis of [Pd(η$^3$-2-methylallyl)(P)$_2$]BF$_4$ complexes (**3**)

#### 5.5.1. Synthesis of (η$^3$-2-methylallyl)bis[diphenyl[(R)-(1)-(phenylethylamino)]phosphine palladium(II) tetrafluoroborate (**3a**)

To 0.24 g (0.61 mmol) of $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(\mu\text{-}Cl)]_2$ and 0.76 g (2.49 mmol) of the phosphine (**a**) dissolved in 20 mL of dichloromethane at 0 °C, 1.24 mmol of a 0.21 M solution of $AgBF_4$ in THF were added. The mixture was stirred for 1 h. After filtering through a Celite pad, the solvent was partially removed. Addition of hexane caused the precipitation of the complex (**3a**) as a brownish solid. This solid was filtrated and washed with ether and pentane. Yield: 0.62 g (58%). $^1$H NMR ($CDCl_3$, 500 MHz): [δ/ppm] 0.95 (d, $J_{HH} = 7.0$, 3 H), 1.03 (d, $J_{HH} = 7.0$, 3H), 1.50 (s, 3H), 3.23 (t, $J_{PH} = 9$, 2H), 3.62 (bs, 1H), 3.68 (bs, 1H), 3.79 (m, 2H), 3.87 (m, 2H), 4.09 (dd, $J_{PH} = 18$, $J_{HH} = 10$, 1H), 4.20 (dd, $J_{PH} = 18$, $J_{HH} = 10$, 1H), 6.95–7.85 (30H). $^{31}$P NMR (101 MHz, $CH_2Cl_2$, 298 K): [δ/ppm] 57.3 (d, $J_{PP} = 47$), 58.4 (d, $J_{PP} = 47$). Anal. Calc. for $C_{44}H_{47}BF_4N_2P_2Pd$: C, 61.52; H, 5.51; N, 3.26. Found: C, 61.46; H, 6.58; N, 3.25%.

#### 5.5.2. Synthesis of (η$^3$-2-methylallyl)bis[diphenyl[(R)-(1-cyclohexylethylamino)phosphine]palladium(II) tetrafluoroborate (**3b**)

This complex was prepared with the same method used for (**3a**). Starting from 1.21 g (3.96 mmol) of the phosphine (**b**), 0.38 g (0.97 mmol) of $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(\mu\text{-}Cl)]_2$ and 8.8 mL (1.94 mmol) of a 0.21 M solution of $AgBF_4$ in THF. The product was obtained as a pale orange solid. Yield: 1.37 g (81%). $^1$H NMR (500 MHz, $CDCl_3$): [δ/ppm] 0.66 (d, $J_{HH} = 6.5$, 3H), 0.75 (d, $J_{HH} = 6.5$, 3H), 1.55 (s, 3H), 0.78–1.75 (22H), 2.72 (bs, 2H), 2.93 (m, 1H), 3.00 (m, 1H), 3.24 (bs, 1H), 3.27 (bs, 1H), 3.63 (s, 1H), 3.69 (s, 1H), 7.09–7.87 (20H). $^{31}$P NMR (101 MHz, $CDCl_3$): [δ/ppm] 56.8 (s). Anal. Calc. for $C_{44}H_{59}BF_4N_2P_2Pd$: C, 60.67; H, 6.83; N, 3.22. Found: C, 61.69; H, 8.0; N, 3.21%.

#### 5.5.3. Synthesis of (η$^3$-2-methylallyl)bis[diphenyl(1-(R)-1-naphtylethylamino)phosphine]palladium(II) Tetrafluoroborate (**3c**)

This complex was prepared with the same method used with (**3a**). Starting from 0.37 g (0.94 mmol) of the phosphine (**c**), 1.35 g (3.79 mmol) of $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(\mu\text{-}Cl)]_2$ and 8.6 mL (1.89 mmol) of a 0.21 M solution of $AgBF_4$ in THF. The product was obtained as a brownish solid. Yield: 1.49 g (83%). $^1$H NMR (400 MHz, $CDCl_3$): [δ/ppm] 0.95 (d, $J_{HH} = 6.4$, 3H), 1.08 (d, $J_{HH} = 6.4$, 3H), 1.46 (s, 3H), 3.27 (d, $J_{PH} = 8.0$, 2H), 3.65 (bs, 1H), 3.67 (bs, 1H), 4.53 (m, 2H), 4.70 (m, 2H), 6.74–7.83 (34H). $^{31}$P NMR (101 MHz, $CDCl_3$): [δ/ppm] 57.7 (d, $J_{PP} = 47.4$), 58.2 (d, $J_{PP} = 47.4$). Anal. Calc. for $C_{52}H_{51}BF_4N_2P_2Pd$: C, 65.12, H, 5.36; N, 2.92. Found: C, 65.54; H, 6.07; N, 2.95%.

#### 5.5.4. Synthesis of (η$^3$-2-methylallyl)bis[phenylbis((R)-1-phenylethylamino)phosphine] palladium(II) tetrafluoroborate (**3d**)

To a solution of $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(\mu\text{-}Cl)]_2$ (0.49 g, 1.25 mmol) in toluene (7 mL) a solution of phenylbis(1-phenylethylamino)phosphine (**d**) (5 mmol) in toluene (7 mL) was added. The mixture was cooled to 0 °C and 2.5 mmol of a solution 0.21 M of $AgBF_4$ in THF was added. The mixture was stirred for 1 h at room temperature. The AgCl formed was filtered and the solvent was removed. The pasty solid obtained was washed and stirred several times with ether until a yellow solid was obtained. Yield: 0.75 g (32%). $^1$H NMR (400 MHz, $CDCl_3$): [δ/ppm] 1.11 (d, $J = 6.8$, 3H), 1.20 (d, $J = 6.8$, 3H), 1.25 (d, $J = 6.8$, 3H), 1.27 (s, 3H), 1.41 (d, $J = 6.8$, 3H), 2.52 (d, $J_{PH} = 11$, 1H), 2.87 (d, $J_{PH} = 11$, 1H), 3.06 (dd, $J = 8.8$, $J = 4$, 1H), 3.14 (t, $J = 9.2$, 1H), 3.54 (m, 1H), 3.66 (m, 1H), 3.70–3.76 (2H), 3.86–3.97 (4H), 6.8–7.6 (30H).$^{31}$P NMR (250 MHz, $CDCl_3$): [δ/ppm] 69.2 (d, $J = 58$), 68.1 (d, $J = 58$ ). Anal. Calc. for $C_{48}H_{57}BF_4N_4P_2Pd \cdot \mathbf{CH_2Cl_2}$: C, 57.13; H, 5.77; N, 5.44. Found: C, 56.01; H, 6.08; N, 5.93%. MS/FAB (+): *m*/*z* 857 $[M]^+$.

#### 5.5.5. Synthesis of (η$^3$-2-methylallyl)bis[phenylbis((R)-1-cyclohexylethylamino)]palladium(II) hexafluorophosphate (**3e**)

To a solution of $[Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)(\mu\text{-}Cl)]_2$ (0.49 g, 1.25 mmol) in $Cl_2CH_2$ (7 mL) a solution of phenylbis(1-cyclohexylethylamino)phosphine (**e**) (5 mmol) in $CH_2Cl_2$ (7 mL) was added. The mixture was cooled to −20 °C and 2.5 mmol of $TlPF_6$ was added. The mixture was stirred at −20 °C for 1 h and then warmed to room temperature and stirred for 1 h. After filtering the TlCl the solvent was removed and the residue was dissolved again in ether. After washing and stirring several times with ether a light yellow powder was obtained. Yield: 1.47 g (86%). $^1$H NMR (400 MHz), $CDCl_3$: [δ/ppm] 0.86 (d, $J = 6.4$, 3H), 0.97 (d, $J = 6.8$, 3H), 1.02 (d, $J = 6.4$, 3H), 1.12 (d, $J = 6.8$, 3H), 1.8–0.8 (44 H), 2.98–2.64 (8H), 3.00 (d, $J = 5.6$, 1H), 3.03 (d, $J = 6$, 1H), 3.25 (bs, 1H), 3.77 (bs, 1H), 7.6–7.5 (10H). $^{31}$P NMR (250 MHz, $CDCl_3$): [δ/ppm] 66.6 (d, $J = 57$), 67.2 (d, $J = 57$). Anal. Calc. for $C_{48}H_{81}BF_6N_4P_3Pd$: C, 56.11; H, 7.95; N, 5.45. Found: C, 56.84; H, 7.95; N, 5.45%. MS/FAB (+): *m*/*z* 881 $[M]^+$.

#### 5.5.6. Synthesis of ($\eta^3$-2-methylallyl)bis(tricyclohexylphosphine)palladium(II) tetrafluoroborate (**3f**)

The complex was prepared following the same procedure described for (**3a**) by using phosphine (**f**). A white solid was obtained after removing the solvent under vacuum and adding hexane. Yield: 0.08 g (19%). $^1$H NMR (200 MHz, $CDCl_3$): [$\delta$/ppm] 0.95–2.06 (69H), 3.08 (bs, 2H), 4.32 (bs, 2H). $^{31}$P (101 MHz, $CH_2Cl_2$), [$\delta$/ppm]: [36.0 (s). Anal. Calc. for $BC_{40}F_4H_{73}P_2Pd$: C, 59.37; H, 9.09. Found: C, 59.49; H, 10.21%.

#### 5.5.7. Synthesis of ($\eta^3$-2-methylallyl)bis(tribenzylphosphine)palladium(II) tetrafluoroborate (**3g**)

This complex was prepared with the same method used with (**3a**). Starting from 0.72 g (2.36 mmol) of the phosphine (**g**), 0.23 g (0.58 mmol) of [Pd($\eta^3$-2-$CH_3C_3H_4$)($\mu$-Cl)]$_2$ and 5.4 mL (1.18 mmol) of a 0.21 M solution of $AgBF_4$ in THF. The product was obtained as a white solid after addition of hexane. Yield: 0.16 g (16%). $^1$H NMR (400 MHz, $CDCl_3$): [$\delta$/ppm] 0.98 (s, 3H), 2.16 (m, 2H), 3.17–3.35 (12H), 3.62 (s, 2H), 7.16–7.34 (30H). $^{31}$P NMR (101 MHz, $CH_2Cl_2$): [$\delta$/ppm] 9.7 (s).

#### 5.5.8. Synthesis of ($\eta^3$-2-methylallyl)bis(dimethylphenylphosphine)palladium(II) Tetrafluoroborate (**3i**)

This complex was prepared with the same method used with (**3a**). Starting from 0.4 mL (2.81 mmol) of the phosphine (**i**), 0.28 g (0.7 mmol) of [Pd($\eta^3$-2-$CH_3C_3H_4$)($\mu$-Cl)]$_2$ and 8.6 mL (1.9 mmol) of a 0.21 M solution of $AgBF_4$ in THF. The product was obtained as a very pale brown oil. $^1$H NMR (250 MHz, $CDCl_3$): [$\delta$/ppm] 1.62 (bs, 12 H), 1.82 (s, 3H), 3.20 (bs, 2H), 4.06 (s, 2H), 7.32 (m, 10H); $^{31}$ P NMR (101 MHz, $CH_2Cl_2$): [$\delta$/ppm] −8.4 (s).

### 5.6. $^{31}$P NMR study of the reactions of [PdCl($\eta^3$-2-methylallyl)(P)] (**2**) with $AgBF_4$ in $CH_2Cl_2$ acetonitrile

To a solution of the appropriate neutral palladium complex **2** (0.44 mmol) and acetonitrile (0.23 mL, 4.4 mmol) in $CH_2Cl_2$ (20 mL) cooled to 0 °C, a solution of $AgBF_4$ (85 mg, 0.44 mmol) in THF (2.1 mL) was added. After stirring for an hour at room temperature the silver chloride was filtered trough a celite pad and the crude product was analysed by $^{31}$P NMR. $^{31}$ P NMR (101 MHz, $CH_2Cl_2$); chemical shift (ppm) and isomer ratio (I/II) for the mixed cationic complexes (**4**): (**4a**): [$\delta$/ppm] 55.6 (s), 57.0 (s), 1.16/1; (**4b**): [$\delta$/ppm] 57.1 (bs); (**4c**): [$\delta$/ppm] 56.2 (s), 57.0 (s); 1/1; (**4d**): [$\delta$/ppm] 67.9 (s), 65.9 (s); 1/1.5; (**4e**): [$\delta$/ppm] 67.1 (bs); (**4f**): [$\delta$/ppm] 42.5 (s); (**4g**): [$\delta$/ppm] 19.8 (s); (**4h**): [$\delta$/ppm] 24.9; (**4i**): [$\delta$/ppm] −4.5; ratio between the mixed cationic complex (**4**) and the bis(phosphine) cationic complex (**3**): **4a/3a**, 1/0.45; **4b/3b**, 1/0.38; **4c/3c**, 1/0.32; **4d/3d**, 1/0.22; **4e/3e**, 1/0.27; **4f/3f**, 1/0; **4g/3g**, 1/0.03; **4h/3h**, 1/0.13; **4i / 3i**,1/0.68.

#### 5.7. Synthesis of acetonitrile ($\eta^3$-2-methylallyl)(tricyclohexylphosphine)palladium(II) tetrafluoroborate (**4f**)

To a solution of 0.40 g (0.84 mmol) of [PdCl($\eta^3$-2-$CH_3C_3H_4$)($PCy_3$)] (**2f**) in 30 mL of $CH_2Cl_2$, 0.22 mL (4.19 mmol) of acetonitrile and 0.84 mmol of $AgBF_4$ in 4 mL of THF are were added. The mixture was stirred for 1 h at −20 °C. The AgCl precipitate formed was filtered off and the solution evaporated to dryness. The oil formed was washed with *n*-pentane several times and 0.23 g (57% yield) of a white precipitate was obtained. $^1$H NMR (250 MHz, $CDCl_3$): [$\delta$/ppm] 1.25–1.89 (m, 33H); 1.99 (s, 3H); 2.47 (s, 3H); 2.61 (bs, 1H), 3.26 (bs, 1H), 3.66 (d, $J = 8.4$, 1H); 4.95 (m, 1H). $^{31}$ P NMR (101 MHz, $CH_2Cl_2$): [$\delta$/ppm] 42.52 (s).

### 5.8. Structure determination

Orange crystals of *cis*-[$PdCl_2$(PPh((*R*)-NHCHCH$_3$-Ph)$_2$)$_2$] (**1**) were obtained by slow diffusion of hexane over dichloromethane solution of the complex at room temperature.

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a MAR345 diffractometer with a image plate detector. Unit-cell parameters were determined from automatic centering of 482 reflections ($3 < \theta < 31°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo K$\alpha$ radiation. 10 285 reflections were measured in the range $3.50 < \theta < 31.62$. 9677 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz-polarization but no absorption corrections were made. The structure was solved by Patterson synthesis, using the SHELXS computer program [42] and refined by the full-matrix least-squares method with SHELX 97 computer program [43], using 10 285 reflections, (very negative intensities were not assumed). The function minimized was $\sum w\|F_o|^2 - |F_c|^2\ |^2$, where $w = [\sigma^2(I) + (0.0920P)^2 + 4.0438P]^{-1}$, and $P = (|F_o|^2 + 2\ |F_c|^2\ )/3$, values of $f$, $f'$ and $f''$ were taken from [44]. The chirality of structure was define from the Flack coefficient, which it is equal to 0.00(5) for the given results [45]. All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom which are linked. The final $R$ (on $F$) factor was 0.054, $wR$ (on $|F|^2$) = 0.152 and goodness-of-fit = 1.047 for all observed reflections. Number of refined parameters was 408. Max. shift/esd = 0.0, Mean shift/esd = 0.0. Max. and min. peaks in final difference synthesis were 0.699 and −0.424 e Å$^{-3}$, respectively.

### 5.9. Hydrovinylation reaction

#### 5.9.1. General procedure

Hydrovinylation reactions were performed in a stainless-steel autoclave fitted with an external jacket connected to an isobutanol bath and the temperature controlled using

a thermostat to ±0.5 °C. Internal temperature was controlled with a termopair and pressure was controlled with a transductor, pressure was registered as a function of time with a Linseis L-200 recorder. The catalyst precursor solution was placed in the autoclave, which had previously been purged by successive vacuum/nitrogen cycles and thermostatted at 15 °C. Ethylene was admitted until a pressure of 15 bar was reached. After the time indicated in Table 6 for each reaction, the autoclave was slowly depressurized and $NH_4Cl$ 10% solution (10 mL) was added. The mixture was stirred 30 min in order to quench the catalyst. The $CH_2Cl_2$ layer was decanted off and dried with $Na_2SO_4$. The quantitative distribution of products and their enantiomeric excess was determined by GC analysis.

*5.9.2. Preparation of catalyst precursor solutions*

*Method A*: To a mixture of 0.03 mmol of the appropriate neutral palladium complex **2** solved in 10 mL of $CH_2Cl_2$, 12.3 mg (0.3 mmol) of acetonitrile and 0.03 mmol of a 0.22 M solution of $AgBF_4$ in THF were added. After stirring in the dark at room temperature for 30 min and filtering off the AgCl formed, 3.45 mL (30 mmol) of styrene were added. The resulting solution was introduced in the reactor previously purged.

*Method B:* To 0.03 mmol of the appropiate neutral palladium complex **2** solved in 10 mL of $CH_2Cl_2$, 3.45 mL (30 mmol) of styrene and 5.85 mg (0.03 mmol) of $AgBF_4$ were added. After stirring in the dark at room temperature for 30 min and filtering off the AgCl formed, the resulting solution was introduced in the reactor.

*Method C*: The complex **4f** (0.03 mmol) and 3.45 mL (30 mmol) of styrene were solved in 10 mL of $CH_2Cl_2$ and introduced in the reactor.

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## Appendix A. Supplementary material

CCDC 633742 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.02.020.

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