The Effect of Chloride Ions on the Mechanism of the Oxidative Addition of Cyclic Allylic Carbonates to Pd^0 Complexes by Formation of Neutral [(η^1-allyl)PdClL$_2$] Complexes

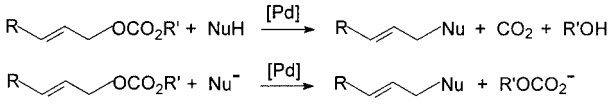
Thibault Cantat,[a] Nicolas Agenet,[a] Anny Jutand,*[a] Roser Pleixats,[b] and Marcial Moreno-Mañas[b]

Keywords: Allyl ligands / Carbonates / Halides / Palladium / Reaction mechanisms

The reversible oxidative addition of a cyclic allylic carbonate *cis*-**1** to palladium(0) complexes ligated by PPh_3 is affected by chloride ions in DMF or chloroform. In the presence of chloride ions, the oxidative addition may become irreversible and the rate of isomerization of *cis*-**1** to *trans*-**1** is slowed down. This is a consequence of a slower isomerization of the cationic complex [(η^3-allyl)Pd(PPh_3)$_2$]$^+$ (*cis*-**2**$^+$) to *trans*-**2**$^+$ due to the formation of neutral [(η^1-allyl)PdCl(PPh_3)$_2$] (*cis*-**3**/*trans*-**3**) complexes. Such complexes are formed instead of the cationic *cis*-**2**$^+$ and *trans*-**2**$^+$ whatever the source of chloride ions, i.e., whether voluntarily added to the cationic complexes *cis*-**2**$^+$ and *trans*-**2**$^+$, voluntarily added in the oxidative addition of *cis*-**1** with Pd^0 complexes ligated to PPh_3, or introduced in the dimeric complexes [(η^3-allyl)Pd(μ-Cl)]$_2$ (*cis*-**5**/*trans*-**5**).

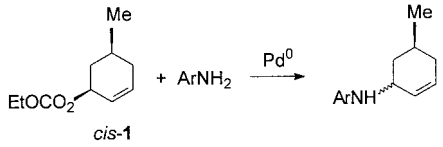
Introduction

Palladium(0) complexes catalyze the substitution of allylic carbonates by neutral or anionic nucleophiles (Scheme 1).[1]



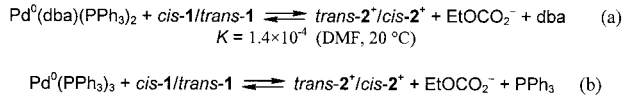
Scheme 1.

It has been established by some of us that the nucleophilic substitution on the cyclic allylic carbonate *cis*-**1** proceeds with a loss of stereospecificity when [Pd^0(PPh_3)$_4$] is the precatalyst (Scheme 2), whereas a nice overall retention of configuration is achieved with [Pd_2(dba)$_3$]/2dppe.[2]

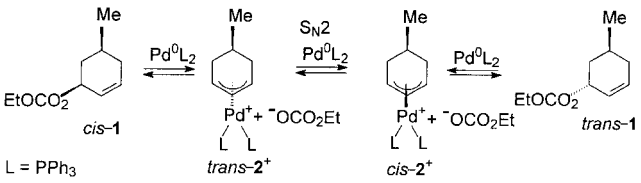


Scheme 2.

The origin of the loss of stereospecificity was determined by investigating the mechanism of the oxidative addition of the cyclic allylic carbonate *cis*-**1** to [Pd^0(PPh_3)$_3$] or [Pd^0(dba)(PPh_3)$_2$], generated from the precursors [Pd^0(PPh_3)$_4$] or {Pd^0(dba)$_2$ and 2 PPh_3} respectively.[3] The oxidative addition was found to be reversible in DMF (Scheme 3), leading to cationic [(η^3-allyl)Pd(PPh_3)$_2$]$^+$ (*trans*-**2**$^+$/*cis*-**2**$^+$) via the common reactive [Pd^0(PPh_3)$_2$] complex (Scheme 4). The overall reaction proceeds with isomerization at the allylic position by isomerization of the intermediate complexes [(η^3-allyl)Pd(PPh_3)$_2$]$^+$ (*trans*-**2**$^+$/*cis*-**2**$^+$) according to an S_N2 mechanism (Scheme 4),[3,4] which is responsible for the loss of stereospecificity. This study also established that the decarboxylation of the ethyl carbonate anion is not as fast as initially postulated.[3,5]



Scheme 3.



Scheme 4.

[a] Ecole Normale Supérieure, Département de Chimie, UMR CNRS-ENS-UPMC 8640
24, Rue Lhomond, 75231 Paris, Cedex 5, France
Fax: +33-1-44323325
E-mail: Anny.Jutand@ens.fr
[b] Departament de Química, Universitat Autonoma de Barcelona, Cerdanyola, 08193 Barcelona, Spain
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

In the case of related *cis* or *trans* cyclic allylic acetates (CO_2Me instead of Me on the cycle), Bäckvall et al. have observed that the stereospecificity of a nucleophilic substitution by Et_2NH is improved when performed in the presence of chloride ions.[4e] The effect of chloride ions on the efficiency, regioselectivity, and enantioselectivity of palladium-catalyzed allylic substitutions has been also reported.[6a–6f]

In 1981, Åkermark et al. reported a difference of reactivity of dimethylamine with an isolated cationic complex $[(\eta^3\text{-allyl})PdL_2]^+BF_4^-$ (L = PPh_3) when compared to the neutral complex $[(\eta^1\text{-allyl})PdClL_2]$, hypothetically generated in situ upon treatment of $[(\eta^3\text{-allyl})Pd(\mu\text{-Cl})]_2$ with 4 equiv. of L. The regioselectivity of the reaction was also affected.[6g] It has been established by some of us that chloride ions, voluntarily added as a salt or introduced by the palladium precursor, play an important role in palladium-catalyzed substitutions of allylic acetates.[7] Indeed, chloride ions modify the kinetics of the oxidative addition of allylic acetates to Pd^0 complexes,[7a] the structure of the allylpalladium(II) complexes generated in the oxidative addition by formation of neutral complexes of the type $[(\eta^1\text{-allyl})PdClL_2]$ (L = PPh_3) instead of cationic $[(\eta^3\text{-allyl})PdL_2]^+$ complexes,[7,8] and the mechanism of the second step of the catalytic cycle, i.e., the nucleophilic attack on allylpalladium(II) complexes, since neutral $[(\eta^1\text{-allyl})PdClL_2]$ complexes were found to react in parallel with cationic $[(\eta^3\text{-allyl})PdL_2]^+$ complexes.[7b]

We report herein that chloride ions also affect the mechanism (kinetics and isomerization) of the oxidative addition of cyclic allylic carbonates to Pd^0 complexes by forming neutral $[(\eta^1\text{-allyl})Pd^{II}]$ chloride complexes.

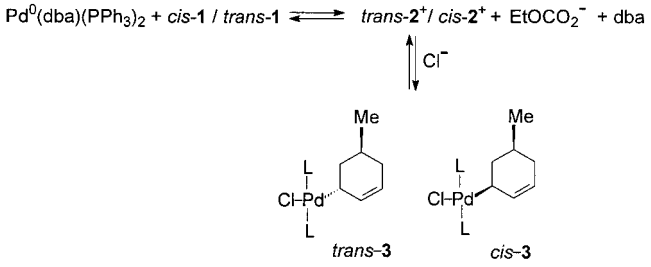
Results and Discussion

Evidence of a Specific Effect of Chloride Ions on the Thermodynamics of the Oxidative Addition of the Cyclic Allylic Carbonate *cis*-1 to Pd^0 Complexes

The complex $[Pd^0(dba)(PPh_3)_2]$, quantitatively generated from a solution of $Pd^0(dba)_2$ (1 mM) and 2 equiv. of PPh_3 in DMF, was characterized by UV spectroscopy by an absorption band at λ_{max} = 396 nm (Figure 1, part a).[9a,9b] Its absorbance decreases slightly with time and is stabilized after addition of 5 equiv. of the cyclic allylic carbonate *cis*-**1** (Figure 1, a), thus attesting that an oxidative addition had taken place (Scheme 3, a).[3] However, the equilibrium in Scheme 3 (a) is not totally shifted to its right-hand side at this concentration of *cis*-**1**. Chloride ions (1, 2, 5, and 10 equiv.) were then added successively using nBu_4NCl as the anion source (Figure 1, a). Successive decreases of the absorbance of $[Pd^0(dba)(PPh_3)_2]$ were observed, thereby suggesting that the chloride ions affect the equilibrium of Scheme 3 (a) by shifting it towards the right-hand side. It is worthwhile to note that $[Pd^0(dba)(PPh_3)_2]$ does not react with chloride ions at the concentrations used above (vide infra).

In order to discriminate between a specific effect of chloride ions due to their coordinating properties and the effect of increasing ionic strength due to the introduction of the ionic species nBu_4N^+ and Cl^- (completely dissociated in DMF), the same UV experiments were done with nBu_4NBF_4, whose anion is not coordinating. A decrease of the absorbance of $[Pd^0(dba)(PPh_3)_2]$ was observed (Figure 1, b), thus indicating that the equilibrium in Scheme 3 (a) is indeed slightly affected by the ionic strength of the medium, which favors the formation of the cationic complexes **2**$^+$. Indeed, the rate of the backward reaction, i.e., the attack of the ethyl carbonate anion on the cationic complexes **2**$^+$, must decrease in an ionic medium due to charge separation.

However, one notices that for the same concentration of added nBu_4NBF_4 or nBu_4NCl, the effect of the latter is much higher (compare Figures 1, parts a and b), which sug-



Scheme 5.

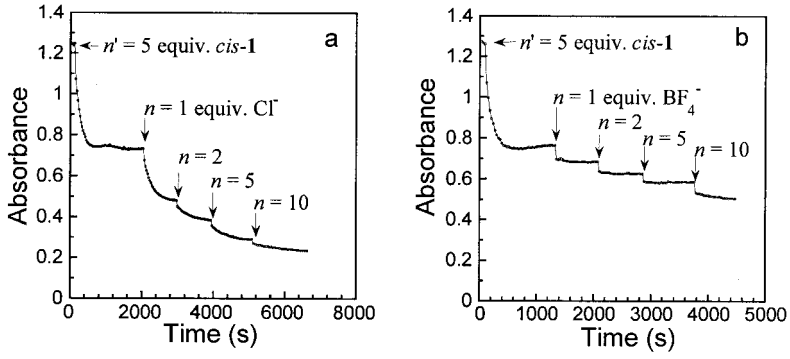


Figure 1. UV spectroscopy at 396 nm in DMF at 20 °C. a) Initial absorbance of $[Pd^0(dba)(PPh_3)_2]$ (1 mM) generated from $Pd^0(dba)_2$ (1 mM) and PPh_3 (2 mM). The arrows indicate the addition of n' = 5 equiv. of *cis*-**1** at t = 100 s and then successive additions of n equiv. of nBu_4NCl. b) The same experiment as in part a of this figure but with addition of nBu_4NBF_4. In both cases, n is the total number of added equivalents.

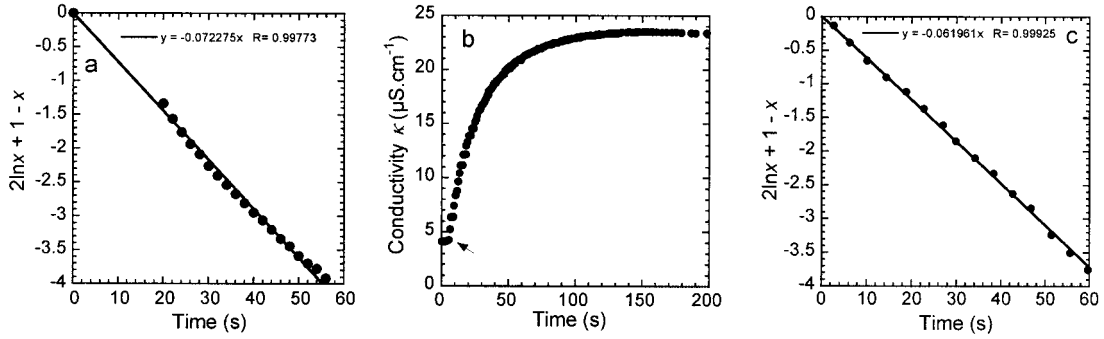
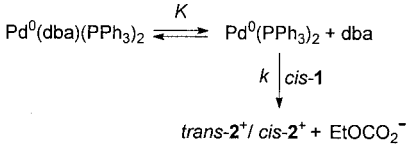


Figure 2. Oxidative addition of *cis*-**1** (0.1 M) to the palladium(0) species generated in situ from $Pd(dba)_2$ (1 mM) and PPh_3 (2 mM) in DMF at 15 °C. a) As monitored by UV spectroscopy: variation of $2\ln x + 1 - x$ vs. time [$x = (D - D_{lim})/(D_0 - D_{lim})$] {$D$: absorbance of $[Pd^0(dba)(PPh_3)_2]$ at time t; D_0: initial absorbance of $[Pd^0(dba)(PPh_3)_2]$; D_{lim}: absorbance at infinite time}. b) Kinetics of the formation of the cationic complex $\mathbf{2}^+\cdot EtOCO_2^-$ generated in the oxidative addition under the same conditions as in part a of this figure, as monitored by conductivity measurements. c) Variation of $2\ln x + 1 - x$ vs. time [$x = (\kappa_{lim} - \kappa)/(\kappa_{lim} - \kappa_0)$] ($\kappa$: conductivity of $\mathbf{2}^+\cdot EtOCO_2^-$ at time t; κ_0: residual initial conductivity; κ_{lim}: final conductivity of $\mathbf{2}^+\cdot EtOCO_2^-$).

gests a *specific* effect of chloride ions on the equilibrium of Scheme 3 (a). At high chloride concentrations (n = 10 equiv.), the residual absorbance is almost reached (Figure 1, a). This suggests a reaction of the chloride ions with the cationic complexes $\mathbf{2}^+$, which generates the new complexes *trans*-**3**/*cis*-**3** (Scheme 5). Such a reaction shifts the equilibrium in Scheme 3 (a) totally towards its right-hand side. The structure of complexes *trans*-**3**/*cis*-**3** will be confirmed later on.

Specific Effect of Chloride Ions on the Kinetics of the Oxidative Addition of the Cyclic Allylic Carbonate *cis*-1 to Pd^0 Complexes in DMF

The reaction of the allylic carbonate *cis*-**1** with $[Pd^0(dba)(PPh_3)_2]$ (1 mM) in DMF was performed with a high concentration of *cis*-**1** (0.1 M) such that the equilibrium in Scheme 3 (a) was totally shifted towards its right-hand side (Scheme 6). The kinetics of the reaction was monitored by UV spectroscopy by recording the decrease of the absorbance of $[Pd^0(dba)(PPh_3)_2]$ at λ = 396 nm with time.



Scheme 6.

The kinetic law of the overall reaction in Scheme 6 is given in Equation (1), where $x = (D - D_{lim})/(D_0 - D_{lim})$ {D = absorbance of $[Pd^0(dba)(PPh_3)_2]$ at time t, D_0 is the initial absorbance of $[Pd^0(dba)(PPh_3)_2]$, and D_{lim} the absorbance at infinite time}.[9c]

$$2\ln x + 1 - x = -kK[cis\text{-}\mathbf{1}]t/C_0 = -k_{obs}t \quad (1)$$

The plot of $2\ln x + 1 - x$ vs. time is linear (Figure 2, a). The value of $k_{obs} = 7.2\times10^{-2}$ s^{-1} was determined from the slope of the straight line and the value of $kK = 7.2\times10^{-4}$ s^{-1} (DMF, 15 °C) as well.

The kinetics of formation of the ionic complexes $\mathbf{2}^+\cdot EtOCO_2^-$ was monitored by conductivity measurements[10] under the same experimental conditions ([*cis*-**1**] = 0.1 M). The kinetic curve is shown in Figure 2, b. The curve is not *S*-shaped, which indicates that the neutral intermediate complex $[(\eta^2\text{-allyl-}OCO_2Et)Pd^0(PPh_3)_2]$, which is supposedly formed in a first complexation step (as observed with acyclic allylic acetates),[10] does not accumulate before its ionization to the cationic complex $\mathbf{2}^+$. In other words, the rate of the ionization step is faster than the rate of the complexation step. Consequently, the rate of formation of the cationic complex $\mathbf{2}^+$, as monitored by conductivity measurements, should be similar to the rate of disappearance of the Pd^0 complex, as monitored by UV spectroscopy (Figure 2, a). Indeed, the plot of $2\ln x + 1 - x$ vs. time [$x = (\kappa_{lim} - \kappa)/(\kappa_{lim} - \kappa_0)$; ($\kappa$: conductivity of $\mathbf{2}^+\cdot EtOCO_2^-$ at time t; κ_0: residual initial conductivity; κ_{lim}: final conductivity of $\mathbf{2}^+\cdot EtOCO_2^-$)] is linear (Figure 2, c). The observed rate constant ($k_{obs} = 6.2\times10^{-2}$ s^{-1} in DMF at 15 °C) was calculated from the slope and was found to be close to the rate of disappearance of the Pd^0 complex ($k_{obs} = 7.2\times10^{-2}$ s^{-1}; vide supra) within the accuracy of both techniques.

In order to anticipate any effect of the ionic strength that might occur when the kinetics of the oxidative addition of *cis*-**1** is investigated in the presence of nBu$_4$NCl, the kinetics was first investigated in the presence of nBu$_4$NBF$_4$ with a concentration in the range 0.3–0.9 M, i.e., at high ionic strength. nBu$_4$NBF$_4$ was added to $[Pd^0(dba)(PPh_3)_2]$ (1 mM) before the addition of *cis*-**1** (0.1 M) and the kinetics was monitored by UV spectroscopy, as in the absence of nBu$_4$NBF$_4$ (vide supra). The rate of the reaction increased slightly upon increasing the nBu$_4$NBF$_4$ concentration. Figure 3 (a) shows the linear variation of $\log(k_{obs}^{BF_4}/k_{obs}^0)$ with the square root of nBu$_4$NBF$_4$ concentration ($k_{obs}^{BF_4}$: observed rate constant in the presence of nBu$_4$NBF$_4$; k_{obs}^0: observed rate constant in the absence of nBu$_4$NBF$_4$, as determined in Figure 2, a), which is in agreement with the Debye–Hückel law, thus attesting that the accelerating effect is indeed due to the ionic strength.[11]

The kinetics of the reaction of allylic carbonate *cis*-**1** (0.1 M) with $[Pd^0(dba)(PPh_3)_2]$ (1 mM) in DMF was then in-

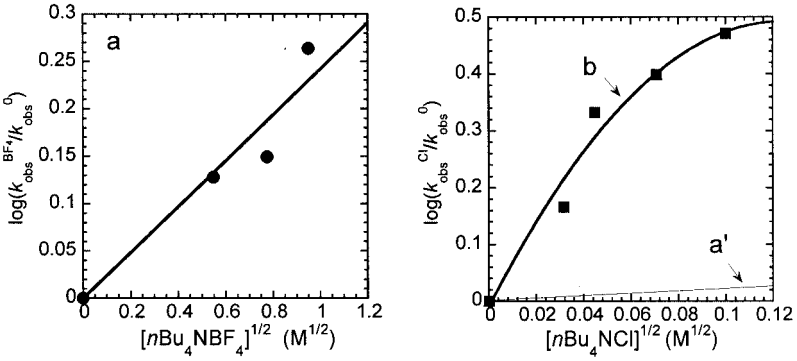
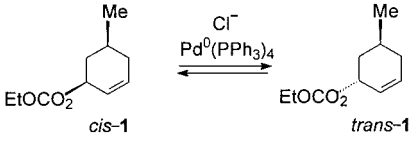


Figure 3. a) Effect of the ionic strength in the reaction of *cis*-**1** (0.1 M) with the Pd^0 complex generated from $Pd(dba)_2$ (1 mM) and PPh_3 (2 mM) in DMF at 15 °C. Variation of $\log(k_{obs}^{BF_4}/k_{exp}^{0})$ vs. the square root of nBu_4NBF_4 concentration. b) Specific effect of chloride ions in the reaction of *cis*-**1** (0.1 M) with the Pd^0 complex generated from $Pd(dba)_2$ (1 mM) and PPh_3 (2 mM) in DMF at 15 °C. Variation of $\log(k_{exp}^{Cl}/k_{exp}^{0})$ vs. the square root of nBu_4NCl concentration. a′) Theoretical effect of the ionic strength due to the presence of nBu_4NCl. The straight line in part a′ of this figure has been rebuilt from the straight line of part a.

vestigated in the presence of various amounts of nBu_4NCl in the range 1–10 mM, i.e., at lower concentrations than that of nBu_4NBF_4 (0.3–0.9 M) in the previous experiments. An accelerating effect was observed that was more pronounced than the one due to the ionic strength. In a first approach, $\log(k_{obs}^{Cl}/k_{obs}^{0})$ (k_{obs}^{Cl}: observed rate constant in the presence of nBu_4NCl; k_{obs}^{0}: observed rate constant in the absence of nBu_4NCl, determined as in Figure 2, a) was plotted against the square root of nBu_4NCl concentration (Figure 3, b). A straight line was not obtained. Each data point could be compared to the expected one due to the effect of the ionic strength. The latter is represented by the straight line in Figure 3 (a′), which was rebuilt from the straight line in Figure 3, a. A comparison of Figures 3 (parts b and a′) shows that, for a similar salt concentration of 0.01 M, the rate of the oxidative addition is 3.4 times faster in the presence of nBu_4NCl than in the presence of nBu_4NBF_4. Consequently, a *specific* effect of chloride ions is observed which might be due to the formation of anionic $[Pd^0(PPh_3)_2Cl]^-$ species[7a] that lead to the neutral $[(\eta^1\text{-allyl})PdCl(PPh_3)_2]$ complexes *trans*-**3**/*cis*-**3**. The accelerating effect is not large because the competition between dba and Cl^- for the coordination of $Pd^0(PPh_3)_2$ is strongly in favor of dba. Indeed, it is only upon addition of a large amount of nBu_4NCl (0.75 M) that 30% of $[Pd^0(dba)(PPh_3)_2]$ (C_0 = 1 mM) disappeared due to the formation of $[Pd^0(PPh_3)_2Cl]^-$, as attested by UV spectroscopy.[7a] At low chloride concentrations, $[Pd^0(PPh_3)_2Cl]^-$ is present at only trace levels.

Specific Effect of Chloride Ions on the Kinetics of the Isomerization of the Cyclic Allylic Carbonate *cis*-1 to *trans*-1 Induced by Pd^0 Complexes

As indicated in Schemes 3 and 4, isomerization of the cyclic allylic carbonate *cis*-**1** to *trans*-**1** is observed in the presence of $[Pd^0(PPh_3)_4]$ or $[Pd^0(dba)(PPh_3)_2]$.[3] The rate of isomerization was monitored by ^1H NMR spectroscopy in $CDCl_3$ by the integration of the signal of the allylic protons of *cis*-**1** and *trans*-**1** located at δ = 5.24 and 5.10 ppm respectively. The same experiment was also performed in the presence of various amounts of chloride ions, added to the Pd^0 complex as nBu_4NCl before the cyclic allylic carbonate *cis*-**1** (Scheme 7).



Scheme 7.

In $CDCl_3$, and starting from a stoichiometric amount of *cis*-**1** and $[Pd^0(PPh_3)_4]$ (20 mM each), the isomerization of *cis*-**1** to *trans*-**1** afforded the thermodynamic ratio 38:62, which was reached within 10 min (curve a in Figure 4), as observed in the first ^1H NMR spectrum recorded. When the same reaction was performed in the presence of a stoichiometric amount of nBu_4NCl (20 mM), the same ratio was also obtained in the first ^1H NMR spectrum (curve b in Figure 4). At these concentrations, the kinetics of the isomerization is too fast to be monitored accurately by ^1H NMR spectroscopy and the effect of chloride ions could not be determined.

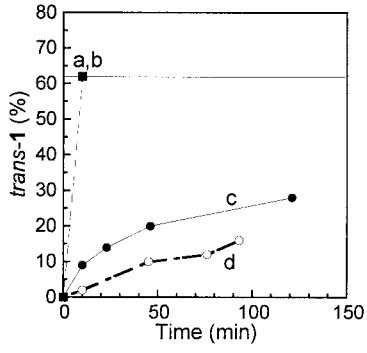
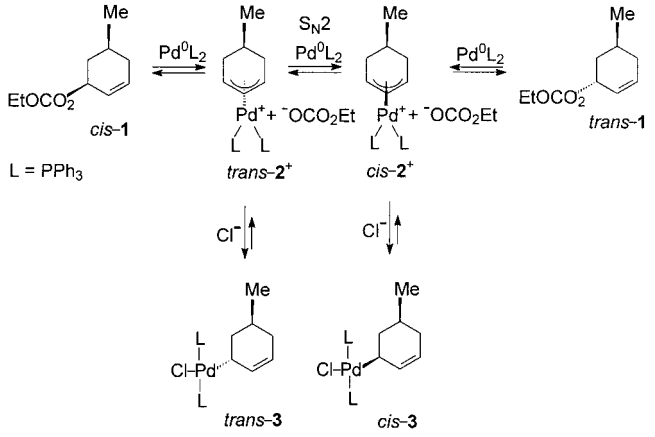


Figure 4. Effect of chloride ions on the kinetics of the isomerization of *cis*-**1** to *trans*-**1** induced by $[Pd^0(PPh_3)_4]$ in $CDCl_3$. a) *cis*-**1** + $[Pd^0L_4]$ (20 mM/20 mM); b) *cis*-**1** + $[Pd^0L_4]$ + Cl^- (20 mM/20 mM/20 mM); c) *cis*-**1** + $[Pd^0L_4]$ + Cl^- (200 mM/20 mM/20 mM); d) *cis*-**1** + $[Pd^0L_4]$ + Cl^- (200 mM/20 mM/200 mM).

When the concentration of *cis*-**1** was increased to 200 mM, the isomerization was slower and the effect of chlo-

rides could be observed, as seen by comparing curves c and d in Figure 4. The isomerization proceeded slower upon increasing the chloride concentration. In another experiment involving [$Pd^0(PPh_3)_4$] (37 mM) and *cis*-**1** (74 mM), the isomerization to *trans*-**1** was complete within 35 min. When the same reaction was performed in the presence of $n$$Bu_4NCl$ (37 mM), an induction period without isomerization was observed. The isomerization started to be significant after 60 min, indicating that the isomerization *cis*-**1** to *trans*-**1** is slowed down in the presence of chlorides.

This inhibiting effect of chloride ions on the rate of isomerization of *cis*-**1** to *trans*-**1** can be explained by the formation of complexes [(η^1-allyl)$PdCl(PPh_3)_2$] (*cis*-**3** and *trans*-**3**; Scheme 8). The formation of such complexes would decrease the rate of the S_N2 isomerization of the cationic complexes *cis*-$\mathbf{2}^+$ and *trans*-$\mathbf{2}^+$ by decreasing their concentration. In other words, part of the palladium catalyst is converted into the neutral complexes *cis*-**3** and *trans*-**3**, which cannot isomerize directly due to the cyclic structure of the η^1-allylic ligand.



Scheme 8.

A *specific* reaction of chloride ions was indeed observed. The reaction was monitored by ^1H NMR spectroscopy performed on a solution of *cis*-**1**, [$Pd^0(PPh_3)_4$], and $n$$NBu_4Cl$ at the same concentration of 20 mM in $CDCl_3$. A fast *cis*-**1**/*trans*-**1** isomerization was observed first (vide supra Figure 4, b). After 4 h, the signals of the allylic carbonates *cis*-**1** and *trans*-**1** were no longer detected (Figure S3 in the Supporting Information) and the free carbonate anion $EtOCO_2^-$ had been released into solution, as attested by the presence of the quadruplet for the CH_2 protons of its Et group at δ = 3.72 ppm (Figure S3). Two new sets of allylic protons were detected whose total integration was one proton, as determined by comparison with the integration of the CH_2 protons of $EtOCO_2^-$ at δ = 3.72 ppm. Close vinylic protons were also observed whose total integration corresponded to two protons (Entry 1 in Table 1, and Figure S3).

These two sets of vinylic and allylic protons do not belong to the known cyclic allylic chlorides *cis*-**4** and *trans*-**4** (see Exp. Sect. and Figure S2), and neither do they belong to the cationic complexes *cis*-$\mathbf{2}^+$ and *trans*-$\mathbf{2}^+$ (Entry 4 in Table 1 and Figure S6), which could have been generated with Cl^- as the counteranion. This strongly suggests the formation of the neutral [(η^1-allyl)$PdCl(PPh_3)_2$] complexes *cis*-**3** and *trans*-**3** (Scheme 9). A ^{31}P NMR spectrum recorded on the same solution did not exhibit the two singlets characteristic of the cationic complexes *cis*-$\mathbf{2}^+$ and *trans*-$\mathbf{2}^+$ (Entry 1 in Table 2) but two new sharp singlets were detected at δ = 23.92 and 23.39 ppm (Entry 2 in Table 2), which were assigned to the neutral complexes *cis*-**3** and *trans*-**3**.

When the oxidative addition of the allylic carbonate *cis*-**1** (20 mM) to [$Pd^0(dba)(PPh_3)_2$] (20 mM), generated from $Pd^0(dba)_2$ + 2 PPh_3, was performed in $CDCl_3$ in the presence of $n$$Bu_4NCl$ (20 mM), the same ^1H NMR spectrum was obtained, thus attesting to the formation of the same complexes *cis*-**3** and *trans*-**3** (Scheme 9).

The following part of this work is devoted to the validation of the mechanism proposed in Scheme 8 by the independent synthesis of the neutral complexes [(η^1-allyl)$PdCl(PPh_3)_2$] (*cis*-**3** and *trans*-**3**).

Synthesis of the Complexes [(η^1-allyl)$PdCl(PPh_3)_2$] (*trans*-**3** and *cis*-**3**) by Treating the Dimer [(η^3-allyl)Pd(μ-Cl)]$_2$ (*trans*,*trans*-**5** and *cis*,*cis*-**5**) with Triphenylphosphane

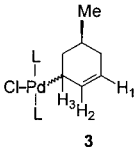
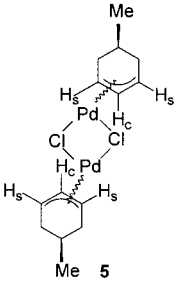
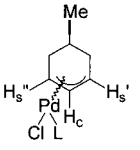
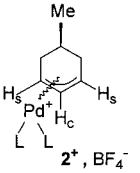
The synthesis of the dimeric complexes **5** was adapted from the Bosnich procedure[12] using a mixture of the cyclic allylic chlorides *cis*-**4** and *trans*-**4** (65:35) (Scheme 10).

The oxidative addition of the Pd^0 generated by reduction of $PdCl_4^{2-}$ by CO was slow, and a large excess of the allylic chlorides was required. The dimeric complex was isolated as a yellow powder and was not very stable, as currently observed in the cyclic series.[4d,13] The ^1H NMR spectrum in $CDCl_3$ (Figure S4 in the Supporting Information) revealed the formation of two complexes *trans*,*trans*-**5** and *cis*,*cis*-**5**, as evidenced by two distinct doublets for the Me group as well as two different sets of signals for the allylic protons H_c and H_s, which were discriminated by a COSY experiment (Entry 2 in Table 1). The *cis* and *trans* structures were assigned by comparison with related complexes reported by Kurosawa et al. (CO_2Me instead of Me)[14] in which the signals of the allylic protons (H_c and H_s) in the *trans* dimer are located at higher field than those of the *cis* complex. The ratio *cis*,*cis*-**5**/*trans*,*trans*-**5** (67:33) was deduced from the ^1H NMR spectrum. The stereochemistry of the oxidative addition of such cyclic allylic chlorides **4** to palladium(0) is not clear and seems to depend strongly on the solvent.[14]

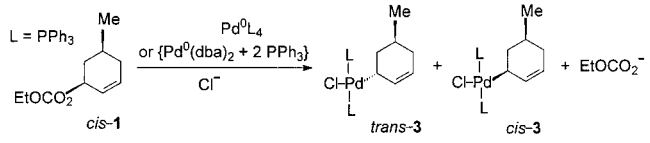
The dimeric complexes *cis*,*cis*-**5**/*trans*,*trans*-**5** (67:33) were treated with PPh_3 (successively PPh_3/Pd = 1, 2, 3) in the absence of any chloride scavenger and the reactions were monitored by ^1H and ^{31}P NMR spectroscopy in $CDCl_3$. Two kinds of complexes were generated depending on the ratio PPh_3/Pd, as attested by their different ^1H and ^{31}P NMR spectra. When the PPh_3/Pd ratio was 1, the mixed complexes *cis*-**6** and *trans*-**6** (70:30) were generated (Scheme 11, Entry 5 in Table 2).

These complexes are the same as those isolated after the oxidative addition of *cis*-**4** and *trans*-**4** (65:35) to the Pd^0

Table 1. ^{1}H NMR spectra (250 MHz vs. TMS) in $CDCl_3$ of the Me protons of the cycle and allylic and/or vinylic protons of allylpalladium complexes.

n		δ (ppm)	δ (ppm)	Scheme
1	 **3**	*cis*-**3** (42 %)[a,b]	*trans*-**3** (58 %)[a,b]	9,[a] 13,15
		0.73 (d, J = 6.5 Hz, 3 H, Me)	0.77 (d, J = 6.5 Hz, 3 H, Me)	
		4.26-4.35 (m, 1 H, H_3)	4.18-4.23 (m, 1 H, H_3)	
		5.75 (dd, J = 8.5, 5 Hz, 1 H, H_1)	5.69 (dd, J = 8.5 Hz, 1 H, H_1)	
		5.84-5.85 (m, H_2)	5.87-5.89 (m, H_2)	
2	 **5**	*trans,trans*-**5** (33 %)	*cis,cis*-**5** (67 %)	10
		0.86 (d, J = 7 Hz, 3 H, Me)	0.88 (d, J = 6.4 Hz, 3 H, Me)	
		4.87 (m, 2H, H_s)	5.06 (dd, J_{HcHs} = 6.2 Hz, $J_{HsH\alpha}$ =	
		5.33 (t, J_{HcHs} = 6.5 Hz, 1 H, H_c)	6.2 Hz, 2H, H_s)	
			5.38 (t, J_{HcHs} = 6.2 Hz, 1 H, H_c)	
3	 **6**	*trans*-**6** (48%)	*cis*-**6** (52 %)	11,12[c]
		0.72 (d, J = 6 Hz, 3 H, Me)	0.76 (d, J = 6 Hz, 3 H, Me)	
		4.10 (m, 1 H, $H_{s'}$)	4.13 (m, 1 H, $H_{s'}$)	
		5.60-5.62 (m, 2 H, H_c,$H_{s''}$)	5.66 (t, J = 7 Hz, 1 H, H_c)	
			5.84 (pseudo q, J = 7 Hz, $H_{s''}$)	
4	 **2$^+$, BF_4^-**	*trans*-**2**$^+$ (66 %)	*cis*-**2**$^+$ (34 %)	14
		0.57 (d, J = 6.4 Hz, 3 H, Me)	0.59 (d, J = 6.5 Hz, 3 H, Me)	
		5.08 (m, 2H, H_s)	5.18 (dd, J_{HcHs} = 6.5 Hz, $J_{HsH\alpha}$ =	
		6.22 (t, J_{HcHs} = 7.3 Hz, 1 H, H_c)	6.5 Hz, 2H, H_s)	
			6.34 (t, J_{HcHs} = 6.5 Hz, 1 H, H_c)	

[a] The *cis*/*trans* ratio is that obtained in the reaction of Scheme 9 with $[Pd^0(PPh_3)_4]$. [b] ^{1}H NMR (400 MHz). [c] The *cis*/*trans* ratio is that obtained in the reaction of Scheme 12.



Scheme 9.

generated from $Pd^0(dba)_2$ + 2 PPh_3 (Scheme 12, Entry 3 in Table 1, Entry 6 in Table 2, Figure S5 in the Supporting Information). Surprisingly, only one phosphane ligand is incorporated into complexes **6**. This is due to the formation of $[PdCl_2(PPh_3)_2]$ (δ =23.4 ppm) as a by-product, which consumes part of the PPh_3 ligand.

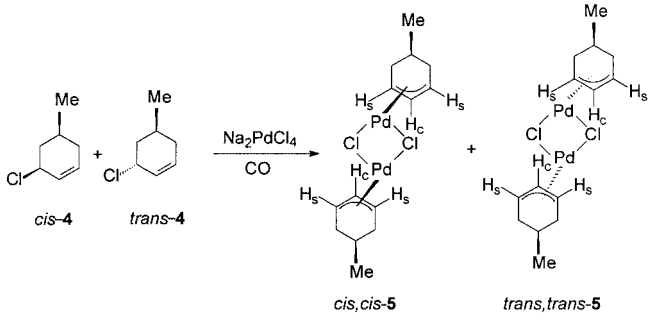
The same complexes *cis*-**6** and *trans*-**6** were also obtained in the oxidative addition of *cis*-**4** and *trans*-**4** (65:35) to $[Pd^0(PPh_3)_4]$ in $CDCl_3$, along with the formation of the allylic phosphonium salts *cis*- and *trans*-**7**$^+$·Cl^-.[16] The formation of the latter from the allylic chlorides *cis*-**4** and *trans*-**4** is catalyzed by Pd^0 complexes.[16]

The protons of the two complexes **6** were assigned from a COSY spectrum and the *cis* and *trans* structures were deduced by comparison with related complexes (CO_2Me instead of Me), which were synthesized by an oxidative addition of the corresponding cyclic allylic chlorides to $[Pd^0(PPh_3)_4]$, as reported by Kurosawa et al.[15]

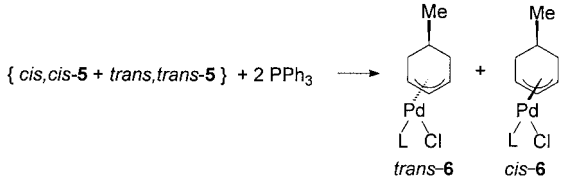
Table 2. ^{31}P NMR shifts (101 MHz vs. H_3PO_4) in $CDCl_3$.

n		Origin	δ [ppm]
1	*cis*-**2**$^+$·BF_4^-	Scheme 14	23.73 (34%)
	trans-**2**$^+$·BF_4^-	Scheme 14	22.85 (66%)
2	*cis*-**3**	Scheme 9	23.92 (42%)
	trans-**3**	Scheme 9	23.39 (58%)
3	*cis*-**3**	Scheme 15	23.92 (44%)
	trans-**3**	Scheme 15	23.40 (56%)
4	*cis*-**3**	Scheme 13	23.90 (43%)
	trans-**3**	Scheme 13	23.38 (57%)
5	*cis*-**6**	Scheme 11	23.91 (70%)
	trans-**6**	Scheme 11	22.97 (30%)
6	*cis*-**6**	Scheme 12	23.91 (55%)
	trans-**6**	Scheme 12	22.97 (45%)
7	*cis*-**7**$^+$·Cl^-/*trans*-**7**$^+$·Cl^-[a]	–	25.9/24.3

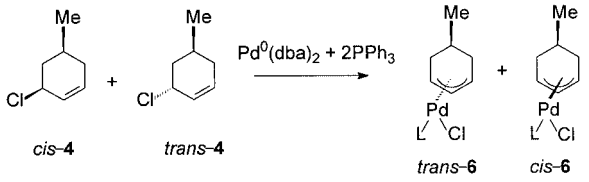
[a] No attempt was made to discriminate the *cis* and *trans* structures.



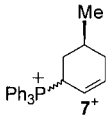
Scheme 10.



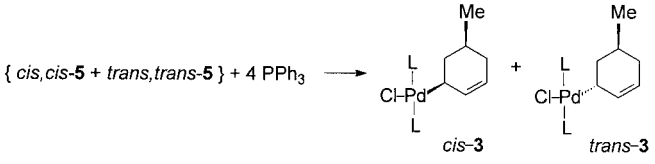
Scheme 11.



Scheme 12.



When the dimeric complexes *cis,cis*-**5**/*trans,trans*-**5** (67:33) were treated with 4 equiv. of PPh_3 per dimer (PPh_3/Pd = 2), two new complexes were generated and assigned as *cis*-**3** and *trans*-**3** (Scheme 13). Indeed, their ^1H and ^{31}P NMR spectra (Entry 1 in Table 1, Entry 4 in Table 2) are the same as those obtained for the complexes generated from the oxidative addition of *cis*-**1** to Pd^0 complexes performed in the presence of added chlorides (Scheme 9).

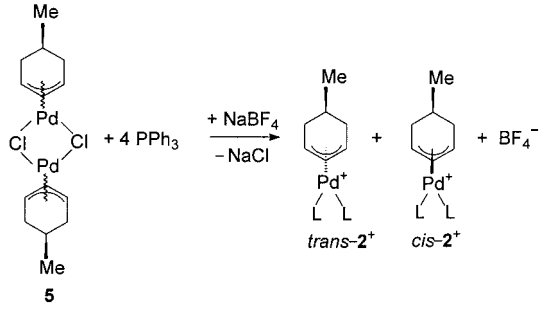


Scheme 13.

The FAB mass spectrum does not contain the peak *m*/*z* = 760 for the complexes *cis*-**3** and *trans*-**3**, but instead one at *m*/*z* = 725 (major one in the isotopic pattern characteristic of the Pd atom) corresponding to the cleavage of Cl^-, as also observed in related complexes.[8e] The detection of a mass peak at *m*/*z* = 630, which corresponds to the fragment $Pd(PPh_3)_2$ after the cleavage of Cl^- and the allylic group, establishes the complexation of the Pd atom by two phosphane ligands in the complexes *cis*-**3** and *trans*-**3**.

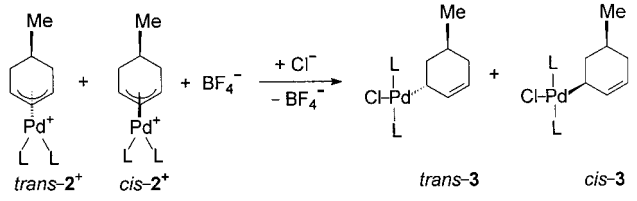
Formation of the Neutral Complexes [(η^1-allyl)PdCl(PPh_3)$_2$] (*cis*-**3** and *trans*-**3**) by Treatment of the Cationic Complexes [(η^3-allyl)Pd(PPh_3)$_2$]$^+$ (*cis*-**2**$^+$ and *trans*-**2**$^+$) with Chloride Ions

The cationic complexes [(η^3-allyl)Pd(PPh_3)$_2$]$^+$ (*cis*-**2**$^+$ and *trans*-**2**$^+$) were synthesized by treating the dimeric complexes *cis,cis*-**5**/*trans,trans*-**5** (67:33) with PPh_3 (PPh_3/Pd = 2) in the presence of $NaBF_4$ as a chloride scavenger, according to a related procedure reported by Powell and Shaw (Scheme 14).[17] The cationic complexes *cis*-**2**$^+$ and *trans*-**2**$^+$ with BF_4^- as the counteranion were isolated and fully characterized by ^1H and ^{31}P NMR spectroscopy (Entry 4 in Table 1, Entry 1 in Table 2, Figure S6 in the Supporting Information), and FAB and electrospray mass spectrometry. Two sets of signals are clearly distinguishable for the allylic protons (central H_c and *syn* H_s), corresponding to the two isomers with a *cis*-**2**$^+$/*trans*-**2**$^+$ ratio of 34:66. According to reports of related complexes,[4d] the protons of the *trans*-**2**$^+$ complex are located at higher field than those of the *cis*-**2**$^+$ complex.



Scheme 14.

When the mixture of the isolated cationic complexes *cis*-**2**$^+$/*trans*-**2**$^+$ (34:66) in $CDCl_3$ was treated with 10 equiv. of Cl^-, the ^1H and ^{31}P NMR spectra changed to those of the neutral complexes [(η^1-allyl)PdCl(PPh_3)$_2$] (*cis*-**3** and *trans*-**3**; Scheme 15) already observed (Scheme 9 and Figure S3). This clearly establishes that the cationic complexes *cis*-**2**$^+$ and *trans*-**2**$^+$ generated in the oxidative addition of *cis*-**1** react with chloride anions to form the neutral complexes *cis*-**3** and *trans*-**3**, as postulated in Scheme 8.

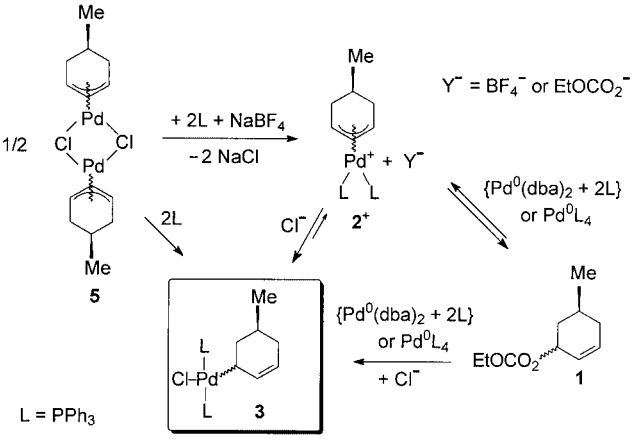


Scheme 15.

Conclusions

It has been shown that whatever the source of chloride ions, i.e. voluntarily added to the cationic complexes *cis*-**2**$^+$

and *trans*-**2**$^+$, voluntarily added during the oxidative addition of *cis*-**1** with Pd^0 complexes ligated to PPh_3, or introduced in the dimeric complexes *cis*- and *trans*-[(η^3-allyl)Pd(μ-Cl)]$_2$ (**5**), the neutral complexes *cis*- and *trans*-[(η^1-allyl)PdCl(PPh_3)$_2$] (**3**) are generated instead of the cationic *cis*- and *trans*-[(η^3-allyl)Pd(PPh_3)$_2$]$^+$ (**2**$^+$) (Scheme 16).



Scheme 16. For clarity, the stereochemistry of the complexes is not shown (see text and Scheme 8).

Therefore, chloride ions play a specific role in the oxidative addition of the cyclic allylic carbonate *cis*-**1** to Pd^0 complexes ligated by PPh_3. Indeed, in the presence of chloride ions: (i) the oxidative addition might become irreversible, (ii) the rate of isomerization of the cyclic allylic carbonate *cis*-**1** to *trans*-**1** is slowed down as a consequence of a slower isomerization of *trans*-**2**$^+$ to *cis*-**2**$^+$, and (iii) neutral [(η^1-allyl)PdCl(PPh_3)$_2$] complexes are formed. Consequently, catalytic reactions performed with the cyclic allylic carbonate *cis*-**1** or *trans*-**1** should be more stereospecific in the presence of chloride ions due to the irreversibility of the oxidative addition and the slower isomerization of *trans*-**2**$^+$ to *cis*-**2**$^+$. This has indeed been observed by Bäckvall et al. in palladium-catalyzed allylic substitutions by the amine Et_2NH with related *cis* or *trans* cyclic allylic acetates (CO_2Me instead of Me on the cycle) when performed in the presence of LiCl, who noted that "*the presence of chlorides led to a remarkable improvement of stereospecificity*" (substitution with retention of configuration).[4d]

Experimental Section

General Methods: All experiments were performed under argon using standard Schlenk techniques. ^{1}H NMR spectra were recorded with a Bruker spectrometer (400 MHz or 250 MHz) with TMS as an internal reference. ^{31}P NMR spectra were recorded with a Bruker spectrometer (101 MHz) with H_3PO_4 as external reference. UV spectra were recorded with a DU 7400 Beckman spectrophotometer. The conductivity was measured with a conductivity meter CDM210 (Radiometer Analytical). The cell constant was 1 cm^{-1}. The conductivity was recorded against time using a computerized home-made program. FAB mass spectra were recorded with a JEOL MS 700 spectrometer with the Magic Bullet matrix. Electrospray mass spectrometry was performed with a T100LC spectrometer (Jeol AccuTOF JMS).

Materials: DMF was distilled from calcium hydride under vacuum and kept under argon. PPh_3 and nBu$_4$NCl were commercial (Acros). Pd(dba)$_2$,[18] [Pd(PPh_3)$_4$],[19] *cis*-**1**,[20] and 5-methyl-2-cyclohexen-1-ol[21] were prepared according to reported procedures.

UV Experiments: These were performed in a thermostatted 1-mm path-length cell on mixtures of Pd^0(dba)$_2$ (1 mM) and 2 equiv. of PPh_3 in DMF with a suitable amount of the allylic carbonate *cis*-**1**, without or with known amounts of nBu$_4$NBF$_4$ or nBu$_4$NCl introduced from a mother solution in DMF.

Conductivity Measurements: Pd(dba)$_2$ (8.6 mg, 0.015 mmol) and PPh_3 (7.9 mg, 0.03 mmol) were added to 15 mL of DMF at 15 °C and the residual conductivity, κ_0, was measured. *cis*-**1** (273 μL, 1.5 mmol) was then added. The conductivity, κ, was measured with time until a constant value, κ_{lim}, was obtained.

Synthesis of 3-Chloro-5-methylcyclohexene (4): This compound was synthesized from the corresponding alcohol[21] according to a published procedure.[22] 5-Methyl-2-cyclohexen-1-ol (4.78 g, 0.043 mol) was dissolved in 55 mL of anhydrous diethyl ether and thionyl chloride (3.21 mL, 0.044 mol) was added. After 1 h the solvent and excess of thionyl chloride were evaporated under vacuum. After distillation (b.p. 42 °C, 15 Torr), 3.35 g of a colorless liquid was collected (60% yield) as a mixture of *cis*-**4** and *trans*-**4** (65:35), whose characterization data were as reported previously.[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (d, J = 6.3 Hz, 3 H, *cis*-Me major), 1.04 (d, J = 6.5 Hz, 3 H, *trans*-Me minor), 1.49 (m, 1 H, MeC*H* in *cis* and *trans*), 1.8 (m, 2 H, CH_2CCl), 2.03–2.23 (m, 2 H, CH_2C= in *cis* and *trans*), 4.59–4.66 (m, 1 H, C*H*Cl in *cis* and *trans*), 5.70–5.91 (m, 2 H, *H*C=C*H* in *cis* and *trans*) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): *cis*-**4**: δ = 21.71, 29.56, 33.06, 42.28, 56.63, 129.21, 129.85 ppm; *trans*-**4**: δ = 21.33, 23.30, 33.55, 40.00, 55.94, 127.23, 131.37 ppm.

Characterization of the Phosphonium Salts *trans*-7$^+$·Cl$^-$ and *cis*-7$^+$·Cl$^-$: Triphenylphosphane (11.5 mg, 0.044 mmol) was dissolved in $CDCl_3$ in an NMR tube along with 3.5 μL (0.026 mmol) of the cyclic allylic chloride *trans*-**4**/*cis*-**4** (35:65) in the presence of 5 mg (0.0087 mmol) of Pd(dba)$_2$. ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 0.92 (d, J = 15 Hz, 3 H, CH_3), 1.45 (m, 1 H, C*H*–Me), 2.2 (m, 4 H, =CCH_2 and CH_2CP$^+$), 5.62 (t, J = 9 Hz, 1 H, C*H*P$^+$), 6.07 (m, 2 H, *H*C=C*H*) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 25.9 (s) and 24.3 (s) ppm in the ratio 72:28. FAB-MS: m/z = 357 [M]$^+$, 262 [M – C_7H_{11} + H]$^+$.

Synthesis of the Dimeric Complexes *trans*,*trans*-5 and *cis*,*cis*-5: Ethanol (4 mL) and 3-chloro-5-methylcyclohexene (**4**; 1.95 g, 8.5 mmol), synthesized as above, were added to sodium tetrachloropalladate (626 mg, 2.1 mmol) in 0.9 mL of degassed water. Carbon monoxide was then bubbled through the solution at 45 °C for 60 min. A yellow precipitate appeared and the solution was kept at –20 °C for 3 d. The yellow precipitate was then filtered, washed with water, ethanol, and diethyl ether, and dried to give 288 mg of a mixture of *trans*,*trans*-**5** and *cis*,*cis*-**5** (58% yield), which was kept at –20 °C in the dark (Figure S4 in the Supporting Information). ***cis*,*cis*-5:** 67% of the mixture. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (d, J = 6.4 Hz, 3 H, Me), 1.48 (m, 3 H), 2.0 (m, 2 H), 5.06 (dd, $J_{Hc,Hs}$ = 6.2, $J_{Hs,H\alpha}$ = 6.2 Hz, 2 H, H_s), 5.38 (t, $J_{Hc,Hs}$ = 6.2 Hz, 1 H, H_c) ppm. ***trans*,*trans*-5:** 33% of the mixture. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (d, J = 7 Hz, 3 H, Me), 1.48 (m, 3 H), 2.0 (m, 2 H), 4.87 (m, 2 H, H_s), 5.33 (t, $J_{Hc,Hs}$ = 6.7 Hz, 1 H, H_c) ppm.

Synthesis of the Cationic Complex *trans*-2$^+$·BF$_4^-$/*cis*-2$^+$·BF$_4^-$: A solution of triphenylphosphane (44 mg, 0.168 mmol) in 5 mL of acetone was added to a solution of the dimer *trans*,*trans*-**5**/*cis*,*cis*-**5** (20 mg, 0.042 mmol) in 6 mL of acetone. Water (2 mL) was then

added followed by a solution of sodium tetrafluoroborate (0.52 g, 4.76 mmol) in 3 mL of water. A grey precipitate of *trans*-**2**$^+$·BF_4^- and *cis*-**2**$^+$·BF_4^- (66:34) was formed and collected by filtration (15 mg, 22% yield). ***trans*-2$^+$·BF_4^-:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.57 (d, J = 6.4 Hz, 3 H, Me), 0.94–1.05 (m, 3 H), 1.57 (m, 2 H), 5.08 (m, 2 H, H_s), 6.22 (t, $J_{Hc,Hs}$ = 7.3 Hz, 1 H, H_c), 7.23–7.40 (m, 30 H, PPh_3) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 22.85 (s) ppm. ***cis*-2$^+$·BF_4^-:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.59 (d, J = 6.5 Hz, 3 H, Me), 0.94–1.05 (m, 3 H), 1.57 (m, 2 H), 5.18 (dd, $J_{Hc,Hs}$ = 6.5, $J_{Hs,H\alpha}$ = 6.5 Hz, 2 H, H_s), 6.34 (t, $J_{Hc,Hs}$ = 6.5 Hz, 1 H, H_c), 7.23–7.40 (m, 30 H, PPh_3) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 23.73 (s) ppm. FAB-MS: m/z = 725 [M], 630 [M – allyl(C_7H_{11})], 463 [M – PPh_3], 368 [Pd(PPh_3)].

Characterization of Complexes *trans*-3 and *cis*-3: These complexes were generated in situ, as shown in Scheme 9, from [$Pd^0(PPh_3)_4$] (11.56 mg, 0.01 mmol), nBu$_4$NCl (2.8 mg, 0.01 mmol), and *cis*-**1** (1.8 μL, 0.01 mmol) in 0.5 mL of $CDCl_3$. The course of the reaction was monitored by ^{1}H NMR spectroscopy. The isomerization *cis*-**1** to *trans*-**1** was observed first. After 4 h, the signals of *cis*-**1** and *trans*-**1** were no longer detectable and the spectrum exhibited the signals of *cis*-**3** and *trans*-**3**. ***cis*-3:** 42%. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.73 (d, J = 6.5 Hz, 3 H, Me), 1.95–2.1 (m, 2 H), 4.26–4.35 (m, 1 H, H_3), 5.75 (dd, J = 8.5, J = 5 Hz, 1 H, H_1), 5.84–5.85 (m, H_2), 7.2–7.5 (m, 18 H, PPh_3), 7.6–7.7 (m, 12 H, PPh_3) ppm. The signals of the aliphatic protons of the cycle are not given due to overlapping with the protons of the $CH_3CH_2CH_2$ chain of nBu$_4$NCl. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 23.92 ppm. ***trans*-3:** 58%. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.77 (d, J = 6.5 Hz, 3 H, Me), 1.95–2.1 (m, 2 H), 4.18–4.23 (m, 1 H, H_3), 5.69 (br. d, J = 8.5 Hz, 1 H, H_1), 5.87–5.89 (m, H_2), 7.2–7.5 (m, 18 H, PPh_3), 7.6–7.7 (m, 12 H, PPh_3) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 23.39 (s) ppm. ESI-MS (methanol): m/z = 725 [M – Cl]$^+$, 630 [M – Cl – allyl(C_7H_{11})].

Characterization of the Complexes *trans*-3 and *cis*-3: These complexes were generated in situ, as shown in Scheme 9, from $Pd^0(dba)_2$ (5.8 mg, 0.01 mmol), PPh_3 (5.6 mg, 0.02 mmol), nBu$_4$NCl (2.8 mg, 0.01 mmol), and *cis*-**1** (1.8 μL, 0.01 mmol) in 0.5 mL of $CDCl_3$. The reaction was monitored by ^{1}H NMR spectroscopy. The isomerization *cis*-**1** to *trans*-**1** was observed first. After 7 h, the signals of *cis*-**1** and *trans*-**1** were no longer detectable and the spectrum exhibited the ^{1}H and ^{31}P NMR signals of *cis*-**3** and *trans*-**3** reported above. A COSY experiment allowed the discrimination between the H_1 and H_2 protons.

Characterization of the Complexes *trans*-3 and *cis*-3: This time these complexes were generated as shown in Scheme 15. A mixture of *trans*-**2**$^+$·BF_4^- and *cis*-**2**$^+$·BF_4^- (66:34; 8 mg, 0.01 mmol), was introduced into an NMR tube containing 0.5 mL of $CDCl_3$, followed by nBu$_4$NCl (28 mg, 0.1 mmol). The ^{1}H and ^{31}P NMR spectra were the same as those reported just above.

Synthesis of the Complexes *trans*-3 and *cis*-3: This time these complexes were generated as shown in Scheme 13. A solution of triphenylphosphane (44.3 mg, 0.169 mmol) in 5 mL of acetone was added to a stirred solution of the dimeric complexes *trans,trans*-**5** and *cis,cis*-**5** (20 mg, 0.0422 mmol) in 10 mL of acetone. After 30 min, the solvent was evaporated. The complexes *trans*-**3** and *cis*-**3** were collected as an orange solid. The ^{1}H and ^{31}P NMR spectra were the same as those reported above.

Synthesis of the Complexes *trans*-6 and *cis*-6: These complexes were generated as shown in Scheme 11. A solution of triphenylphosphane (22 mg, 0.084 mmol) in 5 mL of acetone was added to a stirred solution of the dimeric complexes *trans,trans*-**5** and *cis,cis*-**5** (20 mg, 0.0422 mmol) in 10 mL of acetone. After 30 min, the solvent was evaporated to give 36.4 mg of the complexes *trans*-**6** and *cis*-**6** as an orange solid (86% yield). ***trans*-6:** 48%. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.72 (d, J = 6 Hz, 3 H, Me), 1.0–1.16 (m, 2 H), 1.69–1.87 (m, 2 H), 2.28–2.42 (m, 1 H), 4.10 (m, 1 H, $H_{s'}$), 5.60–5.62 (m, 2 H, H_c, $H_{s''}$), 7.42 (m, 9 H, PPh_3), 7.66 (m, 6 H, PPh_3) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 22.97 (s) ppm. ***cis*-6:** 52%. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.76 (d, J = 6 Hz, 3 H, Me), 1.0–1.16 (m, 2 H), 1.69–1.87 (m, 2 H), 2.28–2.42 (m, 1 H), 4.13 (m, 1 H, $H_{s'}$), 5.66 (t, J = 7 Hz, 1 H, H_c), 5.84 (q, J = 7 Hz, $H_{s''}$), 7.42 (m, 9 H, PPh_3), 7.66 (m, 6 H, PPh_3) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 23.91 (s) ppm.

Characterization of *trans*-6 and *cis*-6: These complexes were generated in situ as shown in Scheme 12. $Pd(dba)_2$ (5 mg, 0.0088 mmol) and PPh_3 (4.6 mg, 0.0017 mmol) were introduced into an NMR tube containing 0.5 mL of $CDCl_3$. The complex [$Pd^0(dba)(PPh_3)_2$], generated in situ, exhibits two broad signals at δ = 27.03 and 24.92 ppm. They disappeared after addition of 1.16 μL (0.0088 mmol) of the allylic chlorides *trans*-**4** and *cis*-**4** (35:65). Two new ^{31}P NMR singlets were observed in $CDCl_3$ at δ = 23.91 and 22.97 ppm (in a 55:45 ratio). The ^{1}H NMR spectrum showed a total consumption of the allylic chlorides and exhibited the signals of complexes *trans*-**6** and *cis*-**6** reported above. The same reaction was performed with [$Pd^0(PPh_3)_4$] (11.5 mg, 0.01 mmol) in $CDCl_3$ under stoichiometric conditions; the same ^{1}H and ^{31}P NMR signals assigned to the complexes *trans*-**6** and *cis*-**6** were observed but the allylic phosphonium salts were also detected as major components.[16] In addition, [$PdCl_2(PPh_3)_2$] (δ = 23.4 ppm) and $OPPh_3$ (δ = 29.1 ppm) were also detected.

Supporting Information: ^{1}H NMR spectra of compounds *cis*-**1**, *cis*-**4**/*trans*-**4**, complexes *cis*-**3**/*trans*-**3**, *cis,cis*-**5**/*trans*-*trans*-**5**, *cis*-**6**/*trans*-**6**, and *cis*-**2**$^+$$BF_4^-$/*trans*-**2**$^+$$BF_4^-$.

Acknowledgments

This work was supported by the Centre National de la Recherche Scientifique, the Ministère de la Recherche et de la Technologie (Ecole Normale Supérieure), and by projects BQU-04002 (MCyT of Spain) and 2001-SGR-00181 (DURSI, Generalitat de Catalunya). This collaborative work was performed under the auspices of COST program D24-0013-02. Johnson Matthey Plc. is greatly thanked for a loan of Na_2PdCl_4.

[1] a) J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, T. Sugiura, K. Takahashi, *J. Org. Chem.* **1985**, *50*, 1523–1529; b) J. Tsuji, *Tetrahedron* **1986**, *42*, 4361–4401; c) S. A. Godleski, in *Comprehensive Organic Synthesis*, vol. 4 (Eds: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**; d) M. Moreno-Mañas, R. Pleixats, in *Handbook of Organopalladium Chemistry for Organic Synthesis* (Ed.: E.-i. Negishi), Wiley, New York, **2002**, vol. II, p. 1707–1767.

[2] M. Moreno-Mañas, L. Morral, R. Pleixats, *J. Org. Chem.* **1998**, *63*, 6160–6166.

[3] C. Amatore, S. Gamez, A. Jutand, G. Meyer, M. Moreno-Mañas, L. Morral, R. Pleixats, *Chem. Eur. J.* **2000**, *6*, 3372–3376.

[4] For postulated and established S_N2 mechanisms, see: a) T. Takahashi, Y. Jinbo, K. Kitamura, J. Tsuji, *Tetrahedron Lett.* **1984**, *25*, 5921–5924; b) P. B. Mackenzie, J. Whelan, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2046–2054; c) H. Kurosawa, S. Ogoshi, N. Chatani, Y. Kawasaki, S. Murai, I. Ikeda, *Chem. Lett.* **1990**, 1745–1748; d) J.-E. Bäckvall, K. L. Granberg, A. Heu-

mann, *Isr. J. Chem.* **1991**, *31*, 17–24; e) K. L. Granberg, J.-E. Bäckvall, *J. Am. Chem. Soc.* **1992**, *114*, 6858–6863 and ref. [3].
[5] F. Ozawa, T. Son, S. Ebina, K. Osakada, A. Yamamoto, *Organometallics* **1992**, *11*, 171–176.
[6] a) J. E. Bäckvall, R. E. Nordberg, *J. Am. Chem. Soc.* **1981**, *103*, 4959–4960; b) R. E. Nordberg, J. E. Bäckvall, *J. Organomet. Chem.* **1985**, *285*, C24; c) M. Kawatsura, Y. Uozumi, T. Hayashi, *Chem. Commun.* **1998**, 217–218; d) G. C. Lloyd-Jones, S. C. Stephen, *Chem. Commun.* **1998**, 2321–2323; e) G. C. Lloyd-Jones, S. C. Stephen, *Chem. Eur. J.* **1998**, *4*, 2539–2549; f) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **1999**, *121*, 4545–4554; g) B. Åkermark, G. Åkermark, L. S. Hegedus, K. Zetterberg, *J. Am. Chem. Soc.* **1981**, *103*, 3037–3040.
[7] a) C. Amatore, A. Jutand, M. A. M'Barki, G. Meyer, L. Mottier, *Eur. J. Inorg. Chem.* **2001**, 873–880; b) T. Cantat, E. Génin, C. Giroud, G. Meyer, A. Jutand, *J. Organomet. Chem.* **2003**, *687*, 365–376.
[8] For η^1-allylpalladium complexes see: a) J. Powell, B. L. Shaw, *J. Chem. Soc. A.* **1967**, 1839–1849; b) P. Fitton, M. P. Johnson, J. E. McKeon, *Chem. Commun.* **1968**, 6–7; c) H. Kurosawa, S. Ogoshi, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 973–984; d) P. Braunstein, F. Naud, A. Dedieu, M.-M. Rohmer, A. DeCian, S. J. Rettig, *Organometallics* **2001**, *20*, 2966–2981; e) M. Kollmar, G. Helmchen, *Organometallics* **2002**, *21*, 4771–4775.
[9] a) C. Amatore, A. Jutand, G. Meyer, *Inorg. Chim. Acta* **1998**, *273*, 76–84; b) C. Amatore, A. Jutand, *Coord. Chem. Rev.* **1998**, *178–180*, 511–528; c) C. Amatore, A. Jutand, F. Khalil, M. A. M'Barki, L. Mottier, *Organometallics* **1993**, *12*, 3168–3178.
[10] A. Jutand, *Eur. J. Inorg. Chem.* **2003**, 2017–2040.
[11] a) As the starting reagents are neutral, the effect of the ionic strength must be in operation at the level of the activated complex; b) P. W. Atkins, *Physical Chemistry*, Oxford University Press, 3rd ed., **1986**, p. 237–245.
[12] a) P. R. Auburn, P. B. Mackenzie, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2033–2046; b) P. B. Mackenzie, J. Whelan, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2046–2054.
[13] a) C. W. Alexander, W. R. Jackson, W. B. Jennings, *J. Chem. Soc. B* **1971**, 2241–2243; b) K. Dunne, F. J. McQuillin, *J. Chem. Soc. C* **1970**, 2196–2200.
[14] H. Kurosawa, S. Ogoshi, Y. Kawasaki, S. Murai, M.-a. Miyoshi, I. Ikeda, *J. Am. Chem. Soc.* **1990**, *112*, 2813–2814.
[15] H. Kurosawa, H. Kajimaru, S. Ogoshi, H. Yoneda, K. Miki, N. Kasai, S. Murai, I. Ikeda, *J. Am. Chem. Soc.* **1992**, *114*, 8417–8424.
[16] Authentic samples of the phosphonium salts *trans*-**7**$^+$ and *cis*-**7**$^+$ with Cl^- as the counteranion were purposely synthesized to detect their possible formation in the reactions investigated in this work. The reaction of the allylic chlorides *trans*-**4** and *cis*-**4** (35:65) with PPh_3 in excess (5 equiv.) was extremely slow. After 3 d, two singlets were observed in the ^{31}P NMR spectrum at δ = 25.9 and 24.3 ppm in $CDCl_3$. The formation of the phosphonium salts is catalyzed by $Pd^0(dba)_2$. With 33% of the catalyst, the allylic chlorides *trans*-**4**/*cis*-**4** (35:65) were totally converted into the phosphonium salts *trans*-**7**$^+$ and *cis*-**7**$^+$. The ^1H NMR spectra of the two salts are very similar, although they could be differentiated by their ^{31}P NMR spectra. However, since these compounds only appear as by-products, their stereochemistry was not investigated.
[17] J. Powell, B. L. Shaw, *J. Chem. Soc. A* **1968**, 774–777.
[18] Y. Takahashi, T. Ito, S. Sakai, Y. Ishii, *Chem. Commun.* **1970**, 1065–1066.
[19] D. T. Rosevear, F. G. H. Stone, *J. Chem. Soc. A* **1968**, 164–167.
[20] M. Moreno-Mañas, J. Ribas, A. Virgili, *J. Org. Chem.* **1988**, *53*, 5328–5335.
[21] a) R. L. Frank, H. K. Hall, *J. Am. Chem. Soc.* **1950**, *72*, 1645–1648; b) J. P. Blanchard, H. L. Goering, *J. Am. Chem. Soc.* **1951**, *73*, 5863–5865.
[22] A. Vallribera, N. Serra, J. Marquet, M. Moreno-Mañas, *Tetrahedron* **1993**, *49*, 6451–6462.

Received: May 12, 2005
Published Online: August 26, 2005

