Importance of the Presence of Chloride Ions in the First Steps of Palladium-Catalyzed Nucleophilic Allylic Substitutions

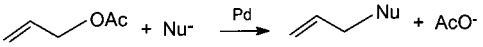
Christian Amatore,*[a] Anny Jutand,*[a] Mohamed A. M'Barki,[a] Gilbert Meyer,[a] and Loïc Mottier[a]

Keywords: Palladium / Halides / Allyl complexes / NMR spectroscopy / Cyclic voltammetry

$[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2 + 4PPh_3$ and $[(\eta^3\text{-}C_3H_5)PdCl(PPh_3)] + 1PPh_3$ do not produce the cationic (π-allyl)palladium(II) complex $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+Cl^-$ but a neutral (σ-allyl)palladium(II) chloride complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ in DMF and THF. This latter complex is also formed when one equivalent of chloride ion is added to $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(BF_4)^-$, leading to the conclusion that $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2 + 4PPh_3$ and $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(BF_4)^-$ are not equivalent precursors for the palladium-catalyzed allylic substitutions when they are performed in the absence of added chloride ions. The (σ-allyl)palladium(II) chloride complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ is also formed instead of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(AcO)^-$ when the oxidative addition of allylic acetate to palladium(0) complexes, such as $[Pd^0(dba)_2] + 2PPh_3$, is performed in the presence of chloride anions. A cationic (π-allyl)palladium(II) complex is thus not formed in the presence of chloride ions, which are either delivered by the catalytic precursor or deliberately added.

Introduction

Palladium(0) complexes catalyze nucleophilic substitutions of allylic acetates (Tsuji−Trost reaction, Equation (1)).[1]



(1)

The main precursors of the palladium(0) catalyst are: **A**: $[Pd^0L_4]$; **B**: $[Pd^0(dba)_2]$ (or $[Pd^0_2(dba)_3] + nL$); **C**: $[(\eta^3\text{-}C_3H_5)PdL_2]^+(BF_4)^-$, a cationic (π-allyl)palladium(II) complex which provides a palladium(0) complex in situ after reaction with the nucleophile; or **D**: $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2 + 4$ L, a dimeric (π-allyl)palladium(II) chloride whose reaction with phosphane ligands is supposed to afford $[(\eta^3\text{-}C_3H_5)PdL_2]^+Cl^-$ and eventually a palladium(0) complex after reaction with the nucleophile.[1] These four different catalytic precursors are often considered to be equivalent, leading to the same active $[Pd^0L_2]$ catalyst and to the same cationic (π-allyl)palladium(II) complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+(AcO)^-$ formed through oxidative addition of $[Pd^0L_2]$ to the allylic acetate. However, recent papers point out that Pd-catalyzed nucleophilic allylic substitutions strongly depend on the precursor of the palladium(0) catalyst in terms of reactivity, regioselectivity and enantioselectivity.[2]

We have already established that $[Pd^0L_4]$ or $[Pd^0(dba)_2]$ associated with phosphane ligands effectively provide the same species $[Pd^0L_2]$, which is active in oxidative additions but is present in low and nonidentical concentrations relative to the precursor concentration because of its endergonic equilibrium with the nonreactive $[Pd^0L_3]$ or $[Pd^0(dba)L_2]$ complexes, respectively.[3] Consequently, $[Pd^0(PPh_3)_4]$ was found to be more efficient than $\{[Pd^0(dba)_2] + 2PPh_3\}$ in allylic nucleophilic substitutions.[4] Conversely, the nucleophilic attack on precursor **C**, the cationic (π-allyl)palladium(II) complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+(BF_4)^-$ is expected to provide $[Pd^0L_2]$ in stoichiometric amounts relative to the precursor. Therefore, the three precursors **A**, **B** and **C** should behave differently in terms of the kinetics of their oxidative addition to an allylic acetate, but should give the same cationic complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+(AcO)^-$, the key intermediate prone to react with the nucleophile.

When considering precursor **D**, i.e., $\{[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2 + 4L\}$, one equivalent of chloride ion is now present although its role is very often neglected. However, this chloride ion may introduce a change in the mechanism. Indeed, we have already established the influence of anions, chloride or acetate, delivered by the precursors of the Pd^0 catalyst on the mechanism of palladium-catalyzed cross-coupling[5a−5c] and Heck reactions.[5b−5d] In this context, it has been observed that deliberately added chloride ions induce stereocontrol in palladium-catalyzed substitutions of cyclic allylic acetates.[6] Recent papers report the beneficial effect of added halides on the regioselectivity of the allylic nucleophilic substitution,[7] as well as on its enantioselectivity.[7b,8] In other cases, a negative effect of added chloride ions on the enantioselectivity has been reported and interpreted as a partial destruction of the memory effect due to the formation of asymmetric ion-pairs between the cationic (π-allyl)palladium(II) complex and acetate anion.[2]

We report here an investigation on the effect of chloride ions on the first steps in the mechanism of palladium-catalyzed allylic substitution, leading to the conclusion that pre-

[a] Ecole Normale Supérieure, Département de Chimie, UMR CNRS 8640,
24, Rue Lhomond, 75231 Paris, Cedex 5, France
Fax: (internat.) + 33-1/4432-3325
E-mail: Anny.Jutand@ens.fr
E-mail: amatore@ens.fr

  1434−1948/01/0303−0873 $ 17.50+.50/0

cursor **D** behaves quite differently from precursors **A**, **B**, and **C**. Cationic (π-allyl)palladium intermediates are not formed from **D** or when chloride anions are voluntary added to any catalytic system **A**, **B** or **C**.

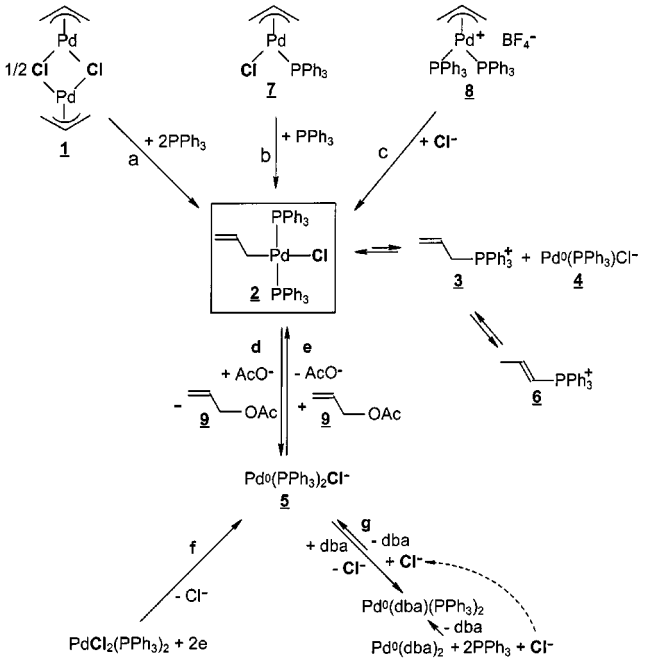
Results and Discussion

Reaction of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (1) with $4PPh_3$ in DMF

When four equivalents of PPh_3 (2 equiv. of L per Pd) were added to a solution of the dimeric (π-allyl)palladium(II) chloride **1** in $CDCl_3$, the three ^1H NMR signals observed for the free complex **1** (Table 1) totally disappeared.

Neither the five signals of $[(\eta^3\text{-}C_3H_5)PdCl(PPh_3)]$ **(7)** (Table 1) nor the three signals of a cationic (π-allyl)palladium(II) $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+Cl^-$ (Table 1) were detected. Instead, a main set of two signals was observed: a quintet (1 H, J = 10 Hz) and a broad doublet (4 H, J = 10 Hz). They are characteristic of the (σ-allyl)palladium chloride complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ **(2)** (Table 1, Scheme 1, route a) as already observed by Shaw et al.[9] Such an NMR pattern is characteristic of a fast equilibrium between two σ forms of **2** [Equation (2)] responsible for the magnetic equivalence of the four CH_2 protons.[9,10]

$$CH_2{=}CH\text{-}C^*H_2\text{-}Pd\text{-}Cl(PPh_3)_2 \rightleftharpoons C^*H_2{=}CH\text{-}CH_2\text{-}Pd\text{-}Cl(PPh_3)_2 \quad (2)$$



Scheme 1. Formation of a (σ-allyl)palladium chloride complex

The ^{31}P NMR spectrum exhibits a single, broad major signal at δ = 20.75 ($\Delta\nu_{1/2}$ = 50 Hz) in DMF and δ = 19.85 ($\Delta\nu_{1/2}$ = 67 Hz) in $CDCl_3$, which is characteristic of the (σ-allyl)palladium chloride complex **2**.

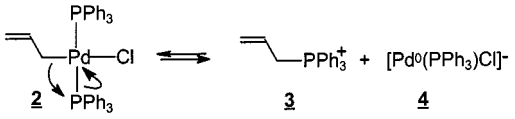
Extra ^1H NMR signals were also observed and assigned to the allytriphenylphosphonium cation **3** (Table 1, Scheme 1) by comparison with an authentic sample of the

Table 1. Characterization of $C_3H_5{-}Pd^{II}$ complexes and $C_3H_5{-}PPh_3^+$ cations (Scheme 1)

	^1H NMR (ppm)[a]	^{31}P NMR (ppm)[b] DMF	THF	E^p_{Red} (volts)[c] DMF
1[d]	3.04 (d, J = 12 Hz, 2 H) 4.12 (d, J = 6.7 Hz, 2 H) 5.46 (t of t, J = 12 and 6.7 Hz, 1 H)	-	-	n.o.
2[e][f][g]	3.72 (br.d, J = 10 Hz, 4 H) 5.62 (quintet, J = 10 Hz, 1 H)	20.75 (br. s)[e] 20.50 (br. s)[f] 20.24 (br. s)[g]		−2.03[g] −2.04[h]
2[e][i]	3.61 (d, J = 10 Hz, 4 H) 5.73 (quintet, J = 10 Hz, 1 H)		11.85 (br. s)[e]	
3[e,f,g]	4.92 (dd, J = 15 and 7 Hz, 2 H) 5.38 (dd, J = 9.5 and 4.5, 1 H) 5.56 (dd, J = 17 and 4.5, 1 H)	22.00 (s)[e] 21.72 (s)[f] 21.74 (s)[g]		−1.54[g] −1.53[h]
6[e,f,g]	2.37 (ddd, J = 6.5, 1.9 and 1.9 Hz, 3 H) 6.60 (ddq J = 22, 16 and 6.5 Hz, 1H) 8.02 (ddq J = 24, 16 and 1.9 Hz, 1H)	19.35 (s)[e] 19.10 (s)[f] 19.12 (s)[g]		
7[d]	2.83 (d, J = 14 Hz, 1 H) 3.11 (d, J = 7 Hz, 1 H) 3.77 (dd, J = 14 and 10 Hz, 1 H) 4.76 (ddd, J = 7, 7 and 1 Hz, 1 H) 5.61 (ddt, J = 14, 14 and 7 Hz, 1 H)	22.77 (s)	22.43 (s)	−1.88
8[d]	3.58 (m, 2 H) 3.97 (bd, J = 6.7 Hz, 2 H) 5.97 (tt, J = 13.5 and 6.7 Hz, 1 H)	23.99 (s)	24.53 (s)	−1.25

[a] 250 MHz; shifts are referred to TMS. Solvent: $CDCl_3$ except [i]. For simplification, aromatic protons are voluntarily omitted. − [b] 163 MHz; shifts are referred to H_3PO_4. The solvent contains 10% [D_6]acetone. − [c] Peak potentials at a gold disk electrode are relative to SCE. Scan rate: 0.2 Vs^{-1} at 20 °C. − [d] Authentic sample. − [e] Formed in reaction of **1** with 4 equiv. PPh_3. − [f] Formed in reaction of **7** with 1 equiv. PPh_3. − [g] Formed in reaction of **8** with 1 equiv. nBu_4NCl. − [h] Formed in the oxidative addition of the electrogenerated $Pd^0(PPh_3)_2Cl^-$ to the allylic acetate **9**. − [i] Solvent: [D_8]THF.

chloride salt **3**·Cl.[12] However, a slight shift of the CH_2-P^+ signal to higher field suggested that chloride was not the counter anion of **3**.[13] Considering that the phosphonium cation **3** was generated from the (σ-allyl)palladium complex **2** by a kind of reductive elimination [Equation (3)], this implies that a palladium(0) complex **4** is also formed concomitantly.



(3)

This interpretation is confirmed by voltammetric data. Indeed, performing cyclic voltammetry in DMF on a solution of **1** (2 mM) and 4 equivalents of PPh_3, revealed the presence of an oxidation peak at −0.03 V which characterizes a palladium(0) complex: it disappeared in the presence of PhI. Moreover, Equation (3) has to be an equilibrium since the ratio **2:3**, (initially equal to 3, as determined from the ^1H NMR spectroscopic data) decreases in the presence of increasing amounts of PPh_3 or dba. The effect of extra PPh_3 or dba is to stabilize the low ligated palladium(0) complex formed in Equation (3) as a more stable complex $[Pd^0(PPh_3)_nCl]^-$ (n = 2, 3)[14] or $[Pd(dba)(PPh_3)_2]$[3] inducing then a shift of the equilibrium in Equation (3) towards its right-hand side.

The conductivity of a solution of **1** (2 mM) and 4 equivalents of PPh_3 was measured in DMF at 20 °C and found to be 78 μS. This shows the formation of ionic species in DMF in agreement with the formulation in Equation (3). The conductivity increases upon successive additions of PPh_3 because of the shift of the equilibrium towards its right hand-side by stabilization of the palladium(0) complex **4** (vide supra). A conductivity of only 2 μS was measured for the same solution in $CDCl_3$, indicating that **4** and **3** (whose ^1H NMR signals are detected in $CDCl_3$) are ion-paired in this less polar solvent.

After two hours, a set of three ^1H NMR signals appeared and were assigned to the 3-propenyltriphenylphosphonium cation **6** by comparison with an authentic sample of **6**·Cl[12] (Table 1, Scheme 1). This cation was formed by the slow isomerization of **3**. The ^{31}P NMR signals of **6** and **3** were also detected in DMF (Table 1) and $CDCl_3$. The stability of **2** strongly depends on the phosphane ligand. The thermodynamic ability of **2** to form phosphonium salts is higher when the phosphane is more basic, consequently the stability of **2** follows the order:

$(p\text{-}CF_3C_6H_4)_3P > (p\text{-}ClC_6H_4)_3P > (p\text{-}HC_6H_4)_3P > (p\text{-}CH_3C_6H_4)_3P$

This set of experiments establishes that addition of four equivalents of PPh_3 per mol of **1** (precursor **D**) does not lead to the expected cationic π-allylpalladium complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+Cl^-$ but to the σ-allylpalladium complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ **(2)** (Scheme 1, route a). This main complex is involved in an equilibrium with a palladium(0) complex, an allylphosphonium salt and a 3-propenylphosphonium salt at longer times (1 h).

The mechanism of the formation of the (σ-allyl)palladium complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ **(2)** cannot be established since no intermediate was observed as its formation from **1** and $4PPh_3$ is too fast. It is known, however, that when only two equivalents of PPh_3 are added to **1**, a neutral (π-allyl)palladium chloride complex $[(\eta^3\text{-}C_3H_5)PdCl(PPh_3)]$ **(7)** is formed.[9] Compound **7** is thus a possible intermediate in the formation of **2**. We have therefore investigated the reaction of **7** with one equivalent of added PPh_3.

Reaction of $[(\eta^3\text{-}C_3H_5)PdCl(PPh_3)]$ (7) with PPh_3 in DMF

Analysis of a solution of **7** containing one equivalent of PPh_3 in $CDCl_3$ or DMF by ^1H and ^{31}P NMR spectroscopy and conductivity measurements showed the same chemical behavior as for the mixture {**1** + $4PPh_3$} (Table 1), i.e., no formation of the cationic (π-allyl)palladium complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+Cl^-$ but formation of the (σ-allyl)palladium chloride complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ **(2)** involved in the equilibrium in Equation (3) (Scheme 1, route b).

Since the cationic (π-allyl)palladium complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+Cl^-$ was not generated, it was of interest to test the reactivity of chloride ions with the cationic (π-allyl)palladium complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+(BF_4)^-$ **(8)**.

Reaction of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(BF_4)^-$ 8 with Chloride Ions in DMF

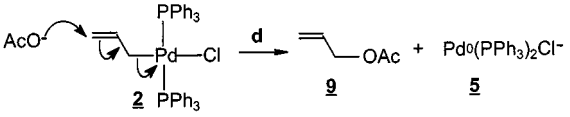
Addition of one equivalent of nBu$_4$NCl to a solution of the cationic (π-allyl)palladium complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+(BF_4)^-$ **(8)** in $CDCl_3$ or DMF induced the complete disappearance of **8** with formation of the (σ-allyl)palladium chloride complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ **(2)** by attack of the chloride ion at the cationic Pd^{II} center (Scheme 1, route c; Table 1). In agreement with the above results, the allyltriphenylphosphonium cation **3** was also formed in this process [Equation (3)].

When less than one equivalent of chloride ion (0.2 equiv.) was added to **8**, the three signals of **8** became broad and overlapped the two signals of **2**. This suggests that the reaction c in Scheme 1 is a dynamic equilibrium lying towards **2** so that it is totally shifted towards the (σ-allyl)palladium chloride **2** as soon as one equivalent of chloride ions are added to **8**.

Reaction of $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ (2) with Acetate Ions in DMF

Acetate anions are continuously released in a palladium-catalyzed substitution at allylic acetates [Equation (1)]. These released acetate ions may conceivably compete with chloride ions for the stabilization of Pd^{II} complexes. We have thus investigated the reaction of acetate ions with the σ-allylpalladium chloride, $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ **(2)**. When one equivalent of nBu$_4$NOAc was added to **2** (preliminarily formed by reaction of **8** with one equiva-

lent of nBu$_4$NCl), the allylic acetate **9** (19%) was observed on the ^{1}H NMR spectrum performed in $CDCl_3$. It was checked independently that nBu$_4$NOAc did not react with commercial **3**·Cl to produce the allylic acetate by a direct nucleophilic substitution. Note, however, that AcO^- catalyzes the isomerization of **3**·Cl to **6**·Cl, but without formation of **9**. This shows that the (σ-allyl)palladium chloride complex **2** is attacked by the acetate ion to produce allylic acetate (Scheme 1, route d), probably by reaction of the acetate anion at the allyl ligand by an S_N2' reaction [Equation (4)].



(4)

This reaction affords an anionic species $[Pd^0(PPh_3)_2Cl]^-$ **(5)**.[14] Such an anionic Pd^0 complex can be generated by reduction of $[PdCl_2(PPh_3)_2]$ (Scheme 1, route f).[14] It was thus of interest to investigate the oxidative addition of **5** to allylic acetate **9**, which is the backward reaction of Equation (4).

Oxidative Addition of $[Pd^0(PPh_3)_2Cl]^-$ to Allylic Acetate in DMF

The electrochemical bielectronic reduction of $[PdCl_2(PPh_3)_2]$ (2 mM in DMF) at −0.88 V produced $[Pd^0(PPh_3)_2Cl]^-$ **(5)** characterized by its oxidation peak at +0.10 V. In the presence of the allylic acetate **9** (4 mM) the oxidation peak current of the electrogenerated palladium(0) decreased, showing a partial reaction of **5** with **9**. This also released AcO^- in solution as characterized by the observation of its oxidation peak at +0.68 V. If the cationic $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(AcO)^-$ **(10)** complex were formed in the oxidative addition, its reduction should be observed at around −1.25 V, which is the reduction potential of an authentic sample of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(BF_4)^-$ **(8)**. Such a reduction peak was not observed, but instead, two reduction peaks were present at more negative potentials, −1.53 V and −2.04 V, showing that the formation of **10** was bypassed. The same couple of reduction peaks was also observed when two equivalents of chloride ions were added to $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(BF_4)^-$ **(8)**, a reaction which affords the (σ-allyl)palladium chloride **2** and the phosphonium cation **3** with $Pd^0(PPh_3)Cl^-$ as the counter-anion [Equation (3]. The reduction peak at −1.53 V was then assigned to the reduction of **3** by comparison with an authentic sample of **3**·Cl, whereas the reduction peak at −2.02 V was assigned to the reduction peak of the (σ-allyl)palladium chloride complex **2**.

This establishes that the oxidative addition of $[Pd^0(PPh_3)_2Cl]^-$ to allylic acetate takes place (backward reaction of Equation (4), route e in Scheme 1) and does not afford the cationic (π-allyl)palladium complex $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(AcO)^-$ **(10)** but the (σ-allyl)palladium chloride $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ **(2)** by the reversible overall reaction shown in Equation (5) (Scheme 1, route f,e,d).[15]

$$Pd^0(PPh_3)_2Cl^- + CH_2{=}CH\text{-}CH_2\text{-}OAc \rightleftharpoons (\eta^1\text{-}C_3H_5)PdCl(PPh_3)_2 + AcO^- \quad (5)$$

However, $[PdCl_2(PPh_3)_2]$ is not often used as a precursor of Pd^0 in allylic substitutions because most nucleophiles active in the allylic substitutions are not able to reduce the Pd^{II} precursor to Pd^0. We have thus investigated the effect of chloride ions on the oxidative addition to allylic acetate starting from another catalytic system: $\{[Pd^0(dba)_2] + 2PPh_3\}$ often used as a precursor of Pd^0 catalysts.[1,16]

Oxidative Addition of $\{[Pd^0(dba)_2] + 2PPh_3\}$ to Allylic Acetate in the Presence of Chloride Ions in DMF

We have established that the oxidative addition of $[Pd^0(dba)_2] + 2PPh_3$ to the allylic acetate **9** is reversible and provides a cationic (π-allyl)palladium complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+(AcO)^-$ **(10)** in DMF (free ions) and in THF (ion pairs) (Equations 6−8).[17] This gives rise to the overall equilibrium in Equation (9) which may be monitored by UV spectroscopy.[17]

$$Pd^0(dba)_2 + 2\,PPh_3 \longrightarrow Pd^0(dba)(PPh_3)_2 + dba \quad (6)$$

$$Pd^0(dba)(PPh_3)_2 \rightleftharpoons Pd^0(PPh_3)_2 + dba \quad (7)$$

$$Pd^0(PPh_3)_2 + CH_2{=}CH\text{-}CH_2\text{-}OAc \rightleftharpoons (\eta^3\text{-}C_3H_5)Pd(PPh_3)_2^+ + AcO^- \quad (8)$$

$$Pd^0(dba)(PPh_3)_2 + CH_2{=}CH\text{-}CH_2\text{-}OAc \rightleftharpoons (\eta^3\text{-}C_3H_5)Pd(PPh_3)_2^+ + AcO^- + dba \quad (9)$$

When nBu$_4$NCl (750 equiv.) was added to a solution of $[Pd^0(dba)_2]$ (1 mM) and $2PPh_3$ in DMF, the absorbance of $[Pd^0(dba)(PPh_3)_2]$ at 396 nm decreased and reached a limiting value (70% of the initial absorbance) establishing the interference of chloride ions in the equilibrium in Equation (7), which is in agreement with the known stability of the anionic complex $Pd^0(PPh_3)_2Cl^-$ [14] [Equation (10)]. It is worthwhile to note that a large amount of nBu$_4$NCl is required to observe a significant decrease of the $[Pd^0(dba)(PPh_3)_2]$ concentration. This indicates that dba is a better ligand for $[Pd^0(PPh_3)_2]$ than Cl^-, and that at low chloride concentration, $[Pd^0(PPh_3)_2Cl]^-$ is only present at trace levels.

$$Pd^0(dba)(PPh_3)_2 + Cl^- \rightleftharpoons Pd^0(PPh_3)_2Cl^- + dba \quad (10)$$

When 60 equivalents of $CH_2{=}CH{-}CH_2{-}OAc$ were added to a solution of $[Pd^0(dba)_2] + 2PPh_3$ in DMF, the absorbance of $[Pd^0(dba)(PPh_3)_2]$ at 396 nm decreased and reached a limiting value corresponding to the thermodynamic

concentration of $[Pd^0(dba)(PPh_3)_2]$ imposed by the equilibrium in Equation (9) (Figure 1a, $t < 70$ s).

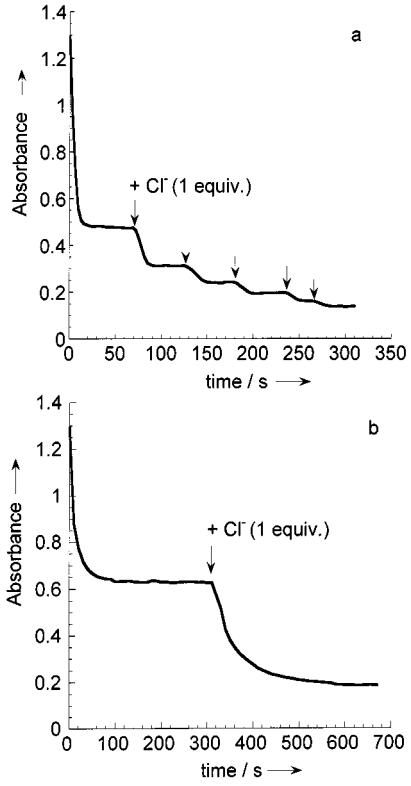


Figure 1. a) Variation of the absorbance ($\lambda = 396$ nm) of the UV spectrum performed in DMF at 20 °C in a 1 mm path cell of a solution of $[Pd^0(dba)_2]$ (1 mmol dm^{-3}) and PPh_3 (2 mmol dm^{-3}) after addition of 60 equivalents of $CH_2{=}CH{-}CH_2{-}OAc$ ($t < 70$ s), followed by successive additions of nBu$_4$NCl (one equivalent at each addition as indicated by the arrows; b) same experiment performed in THF ($\lambda = 394$ nm) after addition of 72 equivalents of $CH_2{=}CH{-}CH_2{-}OAc$ ($t < 300$ s), followed by addition of one equivalent of nBu$_4$NCl as indicated by the arrow

When one equivalent of nBu$_4$NCl was added, the limiting absorbance decreased to a lower value; it again decreased by successive additions of one equivalent of nBu$_4$NCl (Figure 1a). This shows that the chloride anion reacts with $[(\eta^3\text{-}C_3H_5)PdL_2]^+(AcO)^-$ **(10)** formed in the oxidative addition [Equation (9)], shifting this equilibrium to give the total disappearance of $[Pd^0(dba)(PPh_3)_2]$. This reaction gave the (σ-allyl)palladium complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ **(2)** [Equation (11)], which was characterized by performing ^{1}H NMR spectroscopy on a solution of $[Pd^0(dba)_2] + 2PPh_3$ in $CDCl_3$ after addition of **9** (3 equiv.) followed by nBu$_4$NCl (3 equiv.).

$$[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(AcO)^- + Cl^- \longrightarrow (\eta^1\text{-}C_3H_5)PdCl(PPh_3)_2 + AcO^- \quad (11)$$

However, AcO^- anions are released in reaction (11), so that a reaction similar to route d of Scheme 1 should operate, giving rise to the formation of $[Pd^0(dba)(PPh_3)_2]$ as the main Pd^0 complex [Equation (12)] instead of $[Pd^0(PPh_3)_2Cl]^-$.

$$(\eta^1\text{-}C_3H_5)PdCl(PPh_3)_2 + AcO^- + dba \longrightarrow Pd^0(dba)(PPh_3)_2 + CH_2{=}CH\text{-}CH_2\text{-}OAc + Cl^- \quad (12)$$

This has been checked independently by addition of nBu$_4$NOAc (1 equiv.) and dba (2 equiv.) to complex **2** (preliminary formed by reaction of **8** and one equivalent of nBu$_4$NCl). The formation of 19% of allylic acetate was then observed in the ^{1}H NMR spectrum performed in $CDCl_3$, together with $[Pd^0(dba)(PPh_3)_2]$, characterized by its two ^{31}P NMR signals in $CDCl_3$ and DMF[18] [Equation (12)].

Therefore, the oxidative addition of allylic acetate to the palladium(0) generated from $[Pd(dba)_2] + 2PPh_3$ and performed in the presence of chloride ions in DMF is a reversible reaction which affords a (σ-allyl)palladium chloride complex [Equation (13)] and not a cationic (π-allyl)palladium(II) complex $[(\eta^3\text{-}C_3H_5)PdL_2]^+X^-$ (X = Cl or AcO).[19]

$$Pd^0(dba)(PPh_3)_2 + CH_2{=}CH\text{-}CH_2\text{-}OAc + Cl^- \rightleftharpoons (\eta^1\text{-}C_3H_5)PdCl(PPh_3)_2 + AcO^- + dba \quad (13)$$

Formation of $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ in THF

The reaction of the dimeric (π-allyl)palladium(II) chloride **1** with four equivalents of PPh_3 in [D$_8$]THF afforded the (σ-allyl)palladium chloride complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ **(2)** (Table 1, Scheme 1, route a) characterized by its two signals, a quintet (1 H, $J = 10$ Hz) and a doublet (4 H, $J = 10$ Hz) (Table 1) as observed in DMF (vide supra). The ^{31}P NMR spectrum performed in THF exhibited a single, broad major signal ($\Delta\nu = 135$ Hz, Table 1) whose shift strongly depended on the solvent. Indeed, when DMF was added (THF:DMF = 1:1), the ^{31}P NMR signal shifted from $\delta = 11.85$ to 15.35. The phosphonium cation **3** was not observed in pure THF, even at longer times (over 1 h). It is only after addition of two equivalents of dba that the phosphonium cations **3** and **6** could be detected on the ^{31}P NMR spectrum, together with $[Pd^0(dba)(PPh_3)_2]$ ($\delta = 27.34$ and 25.57). This shows that the equilibrium shown in Equation (3) is still operating in THF but is considerably less shifted towards its right-hand side than in DMF, probably because THF is a weaker ligand than DMF for $[Pd^0PPh_3)Cl^-]$ and a weaker solvent for the phosphonium cations **3** and **6**.

Reaction of $[(\eta^3\text{-}C_3H_5)PdCl(PPh_3)]$ **(7)** with one equivalent of PPh_3 or $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(BF_4)^-$ **(8)** with one equivalent of nBu$_4$NCl in THF afforded the (σ-allyl)palladium chloride complex **2** (Scheme 1, route b and c, respectively). As in DMF, no cationic (π-allyl)palladium is formed in THF from **1**, **7**, and **8**, in the presence of chloride ions delivered either by the precursors (**1** or **7**) or deliberately added (to **8**). The three precursors provide the same (σ-allyl)palladium chloride complex **2** (Scheme 1a,b,c).

When 72 equivalents of $CH_2{=}CH{-}CH_2{-}OAc$ were added to a solution of $[Pd^0(dba)_2] + 2PPh_3$ in THF, the absorbance of $[Pd^0(dba)(PPh_3)_2]$ at 394 nm decreased and reached a limiting value corresponding to the thermodynamic concentration of $[Pd^0(dba)(PPh_3)_2]$ imposed in the equilibrium shown in Equation (14) (Figure 1b, $t < 300$ s).[17] This equilibrium is similar to that observed in DMF [Equation (9)] except for the ionic species' ion-pairing.

$$Pd^0(dba)(PPh_3)_2 + CH_2{=}CH{-}CH_2{-}OAc \rightleftharpoons (\eta^3\text{-}C_3H_5)Pd(PPh_3)_2{}^+AcO^- + dba \quad (14)$$

When one equivalent of nBu$_4$NCl was added, the absorbance decreased to almost zero (Figure 1b). This shows that the reaction of one chloride ion with $[(\eta^3\text{-}C_3H_5)PdL_2]^+(AcO)^-$ **(10)** formed in the oxidative addition [Equation (14)] was more efficient than in DMF, shifting this equilibrium to give the total disappearance of $[Pd^0(dba)(PPh_3)_2]$ as soon as one equivalent of Cl^- were added (compare Figure 1a and 1b). This establishes that the reversible overall reaction in Equation (13) is shifted more towards its right-hand side in THF than in DMF.

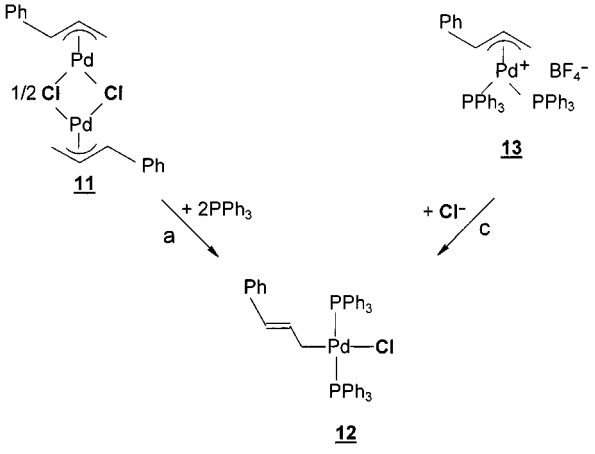
Formation of $[(\eta^1\text{-Ph}-CH{=}CH-CH_2)PdCl(PPh_3)_2]$

When four equivalents of PPh_3 were added to a solution of the dimeric (π-cinnamyl)palladium(II) chloride $[Pd(\eta^3\text{-}Ph-C_3H_4)(\mu\text{-}Cl)]_2$ **(11)** in $CDCl_3$, the four nonaromatic ^{1}H NMR signals characteristic of complex **11** (Table 2) totally disappeared and three new ^{1}H NMR signals were observed and assigned to the (σ-cinnamyl)palladium(II) chloride complex **12** $[(\eta^1\text{-Ph}-CH{=}CH-CH_2)PdCl(PPh_3)_2]$ (Scheme 2, route a).

Table 2. Characterization of cinnamyl−Pd^{II} complexes (Scheme 2)

	^{1}H NMR (ppm)[a]
11[b]	2.97 (d, J = 12 Hz, 1 H) 3.90 (d, J = 6.7 Hz, 1 H) 4.55 (d, J = 11.5 Hz, 1 H) 5.73 (ddd, J = 12, 11.5 and 6.7 Hz, 1 H)
12[c][d]	3.22 (d, J = 10 Hz, 2 H) 5.45 (d, J = 13 Hz, 1 H) 6.10 (dt, J = 10 and 13 Hz, 1 H)
13[b]	3.68 (t, J = 6.5 Hz, 1 H) 3.80 (pseudo t, J = 10 Hz, 1 H) 5.45 (pseudo t, J = 12 Hz, 1 H) 6.41 (m, 1 H)

[a] 250 MHz; shifts are referred to TMS. Solvent: $CDCl_3$. For simplification, aromatic protons are voluntarily omitted. − [b] Authentic sample. − [c] Formed in reaction of **11** with 4 equiv. PPh_3. − [d] Formed in reaction of **13** with 1 equiv. nBu$_4$NCl.



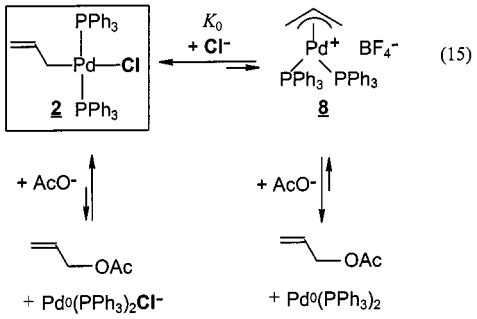
Scheme 2. Formation of a (σ-cinnamyl)palladium chloride complex

This reaction also gives the phosphonium cation $Ph-CH{=}CH-CH_2-PPh_3^+$ (24%) as in the allyl series (see above, Scheme 1). In contrast to the (σ-allyl)palladium(II) chloride complex **2**, which was found to be involved in a fast equilibrium between two σ-forms [Equation (2)], the (σ-cinnamyl)palladium(II) chloride complex **12** is not involved in such an equilibrium (or the equilibrium is very slow) because of the phenyl substituent. Indeed, the ^{1}H NMR spectrum (three different types of non aromatic ^{1}H with an integration of 1:1:2, Table 2) is clearly consistent with a complex of structure $Ph-CH{=}CH-CH_2-PdClL_2$ and not with the isomerized form $Ph-CH(PdClL_2)-CH{=}CH_2$ whose ^{1}H NMR spectrum should exhibit four different non aromatic signals with the same integration.

Complex **12** was also formed when one equivalent of nBu$_4$NCl was added to a solution of the cationic (π-cinnamyl)palladium complex **13** in $CDCl_3$ (Scheme 2, route b) whose four ^{1}H NMR signals were no longer detected (Table 2).

About the Permanence of the Cl^- Effect in the Presence of Increasing Amounts of AcO^- Produced During a Catalytic Reaction

In the case where a catalytic reaction is initiated by the precursor mixture $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ **(1)** + 4PPh_3, the chloride ion concentration is low compared to that of the acetate ions, which are progressively released from the allylic acetate when the catalytic reaction proceeds. One may think that our present results might be affected as a function of the conversion. However, this is not the case. Indeed, it is important to stress that the relative concentration of the (σ-allyl)palladium(II) chloride complex **2** versus the (π-allyl)palladium(II) complex **8** is not affected by the acetate concentration but only depends on the chloride concentration [Scheme 3, reaction (15)].



Scheme 3

The (σ-allyl)palladium(II) chloride complex **2** is quantitatively formed from {**1** + 4PPh_3}, and as well as when one equivalent of Cl^- is added to the cationic complex **8** (see above) so that the equilibrium between **2** and **8** [Scheme 3, Equation (15)] lies considerably in favor of **2** with $K_0\times[Cl^-] >> 100$. The nucleophile may then react with either **2** and **8**, or with both complexes in parallel. In the presence of AcO^-, two competitive reversible reactions occur, which lead to the formation of the allylic acetate (Scheme 3). But provided that reaction (15) in Scheme 3 remains at equilibrium, these reactions do not affect the relative concentration of **2** and **8**, since it only depends on Cl^- concentration

and not on $[Cl^-]/[AcO^-]$. One therefore has: $[\mathbf{2}]/[\mathbf{8}] = K_0 \times [Cl^-] >> 100$, whatever the AcO^- concentration. The effect of AcO^- concentration is only to decrease the absolute concentrations of **2** and **8** but not their ratio, so that the nature of the reactive species, which reacts with the nucleophile, will not be affected by the acetate concentration but will only depend on the intrinsic reactivity of the nucleophile with **2** or **8** and on K_0 and the Cl^- concentration, which determine the respective concentrations of **2** and **8**. When reaction (15) is displaced from its equilibrium by the combined actions of OAc^- and the nucleophile, the kinetic situation becomes much more intricate. The comparative reactivity of a nucleophile with cationic $[(\eta^3\text{-allyl})PdL_2]^+(BF_4)^-$ [20] complexes or with the related complexes $[(\eta^1\text{-allyl})PdClL_2$ is under investigation.

Conclusion

In DMF or THF, the cationic (π-allyl)palladium complex $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+Cl^-$ is not formed from $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2 + 4PPh_3$, $[(\eta^3\text{-}C_3H_5)PdCl(PPh_3)] + 1PPh_3$ or $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(BF_4)^- + 1Cl^-$. Instead, these three precursors lead to the formation of the same (σ-allyl)palladium chloride complex $[(\eta^1\text{-}CH_2{=}CH{-}CH_2)PdCl(PPh_3)_2]$ (Scheme 1a,b,c). Moreover, the latter complex is also formed instead of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(AcO)^-$ when the oxidative addition of palladium(0) complexes to the allylic acetate is performed in the presence of chloride ions, either already ligated to the palladium(0) complex (when $[PdCl_2(PPh_3)_2]$ is the Pd^0 precursor) or deliberately added to a chloride-free palladium(0) complex (when $[Pd(dba)_2] + 2PPh_3$ is the Pd^0 precursor) (Scheme 1f,g,d,e).

This emphasizes the crucial role of presumably "innocent", ligands such as chloride ions, which do not behave as simpler counter-anions of cationic (π-allyl)palladium(II) complexes[2][7b] but modify the chemical structure of reactive intermediates by formation of neutral (σ-allyl)palladium(II) chloride complexes. This also shows that the catalytic precursors of Tsuji–Trost reactions, i.e., $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2 + 4PPh_3$ or $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(BF_4)^-$ are not equivalent since the former system does not lead to the latter complex due to the presence of chloride in its structure. They become equivalent only when chloride ions are added to $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+(BF_4)^-$ but then both provide a neutral (σ-allyl)palladium(II) chloride.

Therefore, among the four catalytic precursors **A**: $[Pd^0L_4]$, **B**: $[Pd^0(dba)_2] + nL$, **C**: $[(\eta^3\text{-}C_3H_5)PdL_2]^+(BF_4)^-$, and **D**: $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2 + 4PPh_3$, the precursor **D** behaves quite differently. Indeed, the intermediate prone to react with the nucleophile is not a cationic (π-allyl)palladium(II) complex, as usually assumed, but a neutral (σ-allyl)palladium(II) chloride. Consequently, this may affect the regioselectivity of the reaction as well as its enantioselectivity in the case of substituted allylic acetates and chiral ligands. The formation of a neutral (σ-allyl)palladium(II) chloride should then be taken into consideration when chloride anions are purposely added to any Pd-catalyzed nucleophilic allylic substitution.

Experimental Section

General Remarks: ^{31}P NMR spectra were recorded on a Bruker spectrometer (101 MHz) using H_3PO_4 as an external reference. – ^1H NMR spectra were recorded on a Bruker spectrometer (250 MHz) using TMS as an internal reference. – UV spectra were recorded on a DU 7400 Beckman spectrophotometer. – Cyclic voltammetry was performed with a home made potentiostat and a wave form generator Tacussel GSTP4. The cyclic voltammograms were recorded on a Nicolet 301 oscilloscope. – Conductivity was measured on a Tacussel CDM210 conductivity meter (cell constant = 1 cm^{-1}).

Chemicals: DMF was distilled from calcium hydride under vacuum and THF from sodium/benzophenone. Commercial allylic acetate $CH_2{=}CH{-}CH_2{-}OAc$ (Acros) was used after filtration through alumina. Commercial (π-allyl)palladium(II)chloride dimer complex, $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (Acros) was used without any purification. $[(\eta^3\text{-}C_3H_5)PdCl(PPh_3)]$,[9] $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$,[17] $[Pd(\eta^3\text{-Ph}{-}C_3H_4)(\mu\text{-}Cl)]_2$ [21] $[Pd(\eta^3\text{-Ph}{-}C_3H_4)(PPh_3)]_2$ [20] and $[Pd(dba)_2]$[22] were prepared according to published procedures.

UV Experiments: These were performed in a thermostated 1 mm path length cell on solutions of $[Pd(dba)_2]$ (11 mg, 0.02 mmol, 1 mmol dm^{-3}) and 2 equivalents of PPh_3 (10 mg, 0.04 mmol) in 20 mL of DMF or THF with the appropriate amount of $CH_2{=}CH{-}CH_2{-}OAc$ and nBu_4NCl (see text and Figure 1).

Electrochemical Set-up and Procedure for Voltammetry: Experiments were carried out in a three-electrode cell connected to a Schlenk line. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge filled with 3 mL of DMF containing nBu_4NBF_4 (0.3 g, 0.3 mol dm^{-3}). Cyclic voltammetry was performed at a steady gold disk electrode (diameter 0.5 mm) with a scan rate of 0.2 V s^{-1} from a solution of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (9 mg, 0.024 mmol) and 4 equivalents of PPh_3 (25 mg, 0.096 mmol) in 12 mL of DMF containing nBu_4NBF_4 (1.2 g, 0.3 mol dm^{-3}).

Acknowledgments

This work has been supported by the Centre National de la Recherche Scientifique (CNRS, UMR 8640) and the Ministère de la Recherche (Ecole Normale Supérieure). We thank Professor H. J. Cristau from Montpellier University for a helpful discussion on the isomerization of allyltriphenylphosphonium cations.

[1] [1a] J. Tsuji, *Palladium Reagents and catalysts*, John Wiley & Sons, Chichester, **1996**, p. 290. – [1b] S. A. Godleski, in *Comprehensive Organic Synthesis, Vol. 4* (Eds: B. M. Trost, I. Flemming), Pergamon, Oxford, **1991**. – [1c] C. G. Frost, J. Howard, J. M. J. Williams, *Tetrahedron: Asymmetry* **1992**, *3*, 1089–1122. – [1d] G. Consiglio, R. Waymouth, *Chem. Rev.* **1989**, *89*, 257–276. – [1e] A. Pfaltz, *Acc. Chem. Rev.* **1993**, *26*, 339–345. – [1f] T. Hayashi, in *Catalytic Asymmetric Synthesis* (Ed: I. Ojima), VCH, New York, **1993**, p. 325. – [1g] B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395–422. – [1h] B. M. Trost, *Acc. Chem. Res.* **1996**, *29*, 355–364.

[2] [2a] G. C. Lloyd-Jones, S. C. Stephen, *Chem. Commun.* **1998**, 2321–2322. – [2b] G. C. Lloyd-Jones, S. C. Stephen, *Chem. Eur. J.* **1998**, *4*, 2539–2549.

[3] [3a] C. Amatore, A. Jutand, F. Khalil, M. A. M'Barki, L. Mottier, *Organometallics* **1993**, *12*, 3168−3178. − [3b] C. Amatore, A. Jutand, G. Meyer, *Inorg. Chim. Acta.* **1998**, *273*, 76−84. − [3c] C. Amatore, A. Jutand, *Coord. Chem. Rev.* **1998**, *178−180*, 511−528.

[4] [4a] D. Ferroud, J. P. Genêt, J. Muzart, *Tetrahedron Lett* **1984**, *25*, 4379−4382. − [4b] W. Oppolzer, J. M. Gaudin, *Helvetica Chim. Acta* **1987**, *70*, 1477. − [4c] S. I. Murahashi, Y. Taniguchi, Y. Imada, Y. Tanigawa, *J. Org. Chem.* **1989**, *54*, 3292−3303.

[5] [5a] C. Amatore, A. Jutand, A. Suarez, *J. Am. Chem. Soc.* **1993**, *115*, 9531−9541. − [5b] C. Amatore, A. Jutand, *J. Organomet. Chem.* **1999**, *576*, 254−278. − [5c] C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, *33*, 314−321. − [5d] C. Amatore, E. Carré, A. Jutand, A. M. M'Barki, G. Meyer, *Organometallics.* **1995**, *14*, 5605−5614.

[6] R. E. Nordberg, J-E. Bäckvall, *J. Organomet. Chem.* **1985**, *285*, C24−C26.

[7] [7a] M. Kawatsura, Y. Uozumi, T. Hayashi, *Chem. Commun.* **1998**, 217−218. − [7b] B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **1999**, *121*, 4545−4555.

[8] U. Burckhardt, M. Baumann, A. Togni, *Tetrahedron: Asymmetry* **1997**, *8*, 155−159.

[9] J. Powell, B. L. Shaw, *J. Chem. Soc. A* **1967**, 1839−1851

[10] A similar NMR pattern was observed when the ^{1}H NMR spectrum of **1** was measured in DMSO in the absence of ligand[11a] as well as for allylmagnesium bromide.[11b]

[11] [11a] J. C. W. Chien, H. C. Dehm, *Chem. Ind.* **1961**, 745−746. − [11b] J. E. Nordlander, J. D. Roberts, *J. Am. Chem. Soc.* **1959**, 1769−1770.

[12] G. Büchi, H. Wüest, *Helv. Chim. Acta* **1971**, *188−189*, 1681−1687.

[13] For commercial **3**·Cl: $\delta(CH_2{-}P^+) = 4.95$ in $CDCl_3$. Since ion pairs were formed in $CDCl_3$, the ^{1}H NMR shift of **3**·Cl is very sensitive to the ionic strength and varies from $\delta = 4.95$ to 4.67 and 4.33 after addition of nBu$_4$NBF$_4$ (0.5 and 2.7 equiv. respectively). The signal position is also sensitive to the counteranion as observed for authentic samples of **3**·Br in $CDCl_3$: $\delta(CH_2{-}P^+) = 4.60$.

[14] C. Amatore, M. Azzabi, A. Jutand, *J. Am. Chem. Soc.* **1991**, *113*, 8375−8384.

[15] This oxidative addition proceeds in two successive reversible steps via a Pd^0 complex ligated to the double bond of the allylic acetate: [15a] C. Amatore, A. Jutand, M. A. M'Barki, L. Mottier, unpublished results. − [15b] M. A. M'Barki, PhD thesis, Paris, **1992**. − [15c] L. Mottier, PhD thesis, Paris **1995**.

[16] For the seminal use of [(Pd(dba)$_2$] with bidentate and then monodentate phosphane ligands in allylic nucleophilic substitutions see: J. C. Fiaud A. Hibon de Gournay, M. Larchevêque, *J. Organomet. Chem.* **1978**, *154*, 175−185 and ref.[4a]

[17] C. Amatore, A. Jutand, G. Meyer, L. Mottier, *Chem. Eur. J.* **1999**, *5*, 466−473.

[18] $\delta = 27.05$ and 24.66 in $CDCl_3$; $\delta = 27.20$ and 25.29 in DMF, see ref. [3]

[19] The (σ-allyl)palladium(II) chloride complex [(η^1-CH_2=CH−CH_2)PdCl(PPh$_3$)$_2$] is also formed in the irreversible oxidative addition of the allylic chloride CH_2=CH−CH_2−Cl to a solution of [Pd(dba)$_2$] and two equivalents of PPh$_3$.

[20] O. Kuhn, H. Mayr, *Angew. Chem. Int. Ed.* **1999**, *38*, 343−346.

[21] P. R. Auburn, P. B. Mackenzie, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2033−2046.

[22] Y. Takahashi, T. Ito, S. Sakai, Y. Ishii, *J. Chem. Soc., Chem. Commun.* **1970**, 1065−1066.

Received July 24, 2000
[I00289]