Evidence of the Reversible Formation of Cationic π-Allylpalladium(II) Complexes in the Oxidative Addition of Allylic Acetates to Palladium(0) Complexes

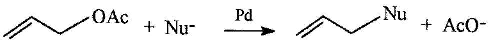
Christian Amatore,* Anny Jutand,* Gilbert Meyer, and Loïc Mottier[a]

Abstract: It has been established that the oxidative addition of allylic acetate with the palladium(0) complex, generated from a mixture of $Pd(dba)_2 + 2\,PPh_3$, affords a cationic π-allylpalladium(II) complex. This reaction is reversible and proceeds through at least two successive equilibria. The overall equilibrium constant has been determined in THF and DMF. The acetate ion does not act as a simple leaving group, but plays the role of a nucleophile able to react with cationic π-allylpalladium(II) complexes to reproduce the allylic acetate; a process that may be responsible for the racemization of chiral allylic acetates. In DMF, no significant ion pairing occurs and free ions are formed. On the other hand, in THF almost complete ion pairing occurs and almost no free ions are produced.

Keywords: allyl complexes · cations · mechanistic studies · palladium · reversible oxidative addition

Introduction

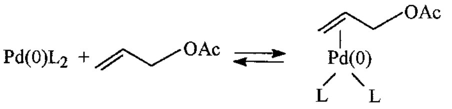
Palladium complexes are efficient catalysts in reactions involving nucleophilic substitutions on allylic acetates [Eq. (1)] or their derivatives (Tsuji–Trost reactions).[1–2] Chiral ligands on the palladium may induce enantioselective reactions.[2]



(1)

Two kinds of catalysts are generally used, either palladium(0) complexes or π-allylpalladium(II) complexes. Oxidative addition of palladium(0) with the allylic acetate is admittedly supposed to be the first step of the catalytic cycle and to proceed in two successive reactions. The first one is a coordination of a low-ligated palladium(0) complex Pd^0L_2 (L = phosphine ligand) to the double bond of the allylic acetate [Eq. (2)] followed by an oxidative addition in which a cationic π-allylpalladium(II) complex is formed [Eq. (3)] with release of the leaving group AcO^-.

As a result of the nucleophilic attack on the cationic π-allylpalladium(II) complex, a palladium(0) complex is regenerated [Eq. (4)]; this may then initiate a second catalytic cycle through Equations (2) and (3).



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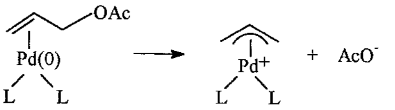

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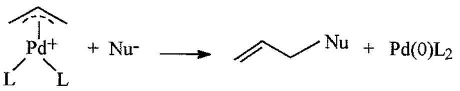

(4)

The feasibility of reaction shown in Equation (4) has been well established by treating nucleophiles on authentic samples of cationic π-allylpalladium(II) complexes,[1–2] which are efficient catalysts as they are precursors of palladium(0) complexes through Equation (4). A cationic π-allylpalladium(II) complex was thus postulated as resulting from the oxidative addition [Eq. (3)], although to our knowledge no evidence of its formation under true catalytic conditions has been reported. In this context, it is worth recalling that cationic π-allylpalladium(II) complexes are usually not synthesized by an oxidative addition of allylic acetates with palladium(0) complexes.[3] They are generally synthesized

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independently by reacting MBF_4 or $MBPh_4$ ($M = Na, K$) with the π-allylpalladium(II) chloride dimeric complex, $[\{Pd(\eta^3-C_3H_5)(\mu\text{-}Cl)\}_2]$, in the presence of the ligand L.[4] Under these conditions, the counter anion is BF_4^- (or BPh_4^-), that is, not OAc^- as it should be when the oxidative addition is performed from allylic acetates. Consequently, the possible role of the acetate ion (or of another leaving group) in the overall catalytic process has been generally omitted. Moreover, in some cases, it is more convenient to start from a cationic π-allylpalladium(II) complex expected to be formed in situ from a mixture of $[\{Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$ and the ligand L. This reaction generates one chloride ion per palladium center, but it is noteworthy that the role of the chloride ions is very often neglected.[5]

Our target is to understand the mechanism of the Pd-catalyzed nucleophilic substitution on allylic acetates better, yet having in mind a more ambitious long-term objective, that is, to understand the origin of the enantioselectivity achieved in the presence of chiral ligands. This approach requires a detailed mechanistic analysis of every step of the catalytic cycle, independently but also in the context of the overall catalytic reaction, that is, taking in account all the species in solution such as anions [the leaving group of the allylic derivative or the anions provided by the precursor of the palladium(0)] or cations (provided by the nucleophile). Indeed we have shown in previous contributions that these generally omitted ions play in truth crucial kinetic roles.[6] In this context, it is worth to recall that Trost et al. have established that mixing a chiral allylic acetate with a palladium(0) complex ligated by triphenylphosphine, without any nucleophile, resulted in a partial racemization of the allylic acetate.[7] Such racemization might be responsible for the loss of stereospecificity observed in some palladium-catalyzed allylic substitutions.[8] This suggests that both of the reactions in Equations (2) and (3) are reversible and that the acetate ion is able to attack the intermediate cationic π-allylpalladium complex, resulting in the inversion of the initial configuration of the chiral allylic acetate. These results encouraged us to investigate in detail the mechanism of the oxidative addition of palladium(0) complexes with allylic acetate under experimental conditions close to those of a catalytic reaction. Among the various precursors of palladium(0) complexes, mixtures of $Pd^O(dba)_2$ (dba = *trans,trans*-dibenzylidenacetone) and phosphine ligands L, afford efficient catalysts.[1, 2, 9] Indeed $Pd(dba)_2$ is air stable and it allows an easy investigation of the role of different phosphine ligands in catalytic reactions just by mixing $Pd(dba)_2$ and the desired ligand. We have previously identified the effective palladium(0) catalytic species generated in situ in mixture of $Pd(dba)_2 + 2L$ (L = monodentate phosphine ligands)[10] by investigating the mechanism of the oxidative addition with phenyl iodide. In DMF and THF solvents (noted S hereafter), the scheme shown in Equations (5)–(7) has been established.[10]

$$Pd^0(dba)_2 + 2L \longrightarrow Pd^0(dba)L_2 + dba \qquad (5)$$

$$Pd^0(dba)L_2 + S \rightleftharpoons SPd^0L_2 + dba \qquad (6)$$

$$SPd^0L_2 + PhI \longrightarrow PhPdIL_2 + S \qquad (7)$$

$Pd^O(dba)L_2$ is the major complex in solution, but the reactive species is the low ligated complex SPd^OL_2. However its concentration is always very low due to its up-hill involment in the very endergonic equilibrium (6), thus resulting in a slow overall reactivity. Indeed this catalytic system was found to be less reactive than Pd^OL_4 ($L = PPh_3$) emphasizing the negative role of the dba ligand in the overall reactivity, due to its strong affinity for SPd^OL_2.

We report here our investigation on the mechanism of the oxidative addition of allylic acetates with palladium(0) complex generated in situ in mixtures of $Pd(dba)_2 + 2PPh_3$. Our main contribution is to demonstrate kinetically for the first time that i) the complex formed in the oxidative addition is really a cationic π-allylpalladium(II) complex and (ii) the oxidative addition is reversible, evidencing that AcO^- is not only a simple leaving group as generally postulated, but that it might play another role in the catalytic process.

Abstract in French: *L'addition oxydante de l'acétate allylique avec le complexe du palladium(0) formé in situ dans le mélange $Pd(dba)_2 + 2PPh_3$ donne un complexe π-allylpalladium(II) cationique. Cette réaction est réversible et résulte de deux équilibres successifs. La constante de l'équilibre global a été déterminée dans le THF et le DMF. L'ion acétate n'est donc pas un simple groupe partant mais joue aussi le rôle de nucléophile capable de réagir avec le complexe π-allylpalladium(II) cationique pour redonner l'acétate allylique. Cette réaction pourrait être à l'origine de la racémisation de divers acétates allyliques chiraux. Dans le DMF, on obtient des ions libres alors que des paires d'ions sont formées dans le THF.*

Results and Discussion

Evidence of the nucleophilic attack of an acetate ion on a cationic π-allylpalladium complex by ^1H and ^{31}P NMR spectroscopy: ^1H NMR (250 MHz, TMS) spectroscopy performed on an authentic sample of the π-allylpalladium complex $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ in $[D_1]$chloroform exhibited, besides the aromatic proton of PPh_3, three sets of signals (Figure 1a) at $\delta = 5.97$ (1H, Hc), $\delta = 3.97$ (2H, Hb), and $\delta = 3.58$ (2H, Ha). After addition of one equivalent of nBu_4NOAc and two equivalents of dba, the signals Hc, Hb, and Ha, corresponding to the π-allylpalladium complex became broader (Figure 1b), while a new set of thin signals appeared that were characteristic of the allylic acetate $CH_2{=}CH{-}CH_2{-}OAc$ (compare with the spectrum of an authentic sample of $CH_2{=}CH{-}CH_2{-}OAc$ shown in Figure 1c). The $OCOCH_3$ protons of $CH_2{=}CH{-}CH_2OAc$ were also detected as a thin singlet at $\delta = 2.09$, while those of $CH_3CO_2^-$ appeared as a broad singlet at $\delta = 1.98$.

^{31}P NMR (101 MHz, H_3PO_4) spectroscopy performed on a mixture of $Pd^O(dba)_2$, two equivalents of PPh_3, and fifty equivalents of $CH_2{=}CH{-}CH_2OAc$ in DMF exhibited, besides

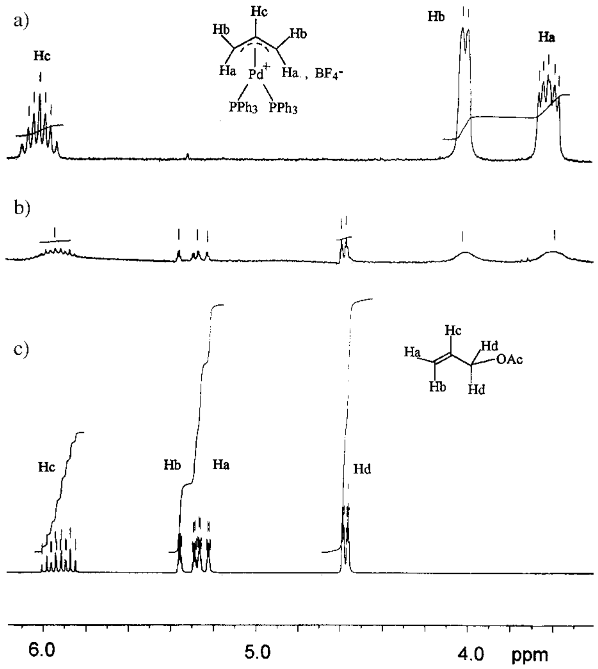


Figure 1. ^{1}H NMR spectrum (250 MHz, [D$_1$]chloroform, TMS). a) [(η^3-C_3H_5)Pd(PPh_3)$_2$][BF_4]. b) [(η^3-C_3H_5)Pd(PPh_3)$_2$][BF_4], 2 equiv of dba, and 1 equiv of nBu$_4$NOAc. c) CH_2=CH–CH_2–OAc.

the two signals of Pd^0(dba)(PPh_3)$_2$ at $\delta_1 = 27.36$ and $\delta_2 = 25.53$,[10a] a broad signal at $\delta_3 = 24.06$ (Figure 2a). The latter was assigned to the cationic π-allylpalladium complex ion (η^3-C_3H_5)Pd(PPh_3)$_2^+$ by comparison with an authentic sample of [(η^3-C_3H_5)Pd(PPh_3)$_2$][BF_4].[11] ^{31}P NMR spectroscopy performed on an authentic sample of the π-allylpalladium complex [(η^3-C_3H_5)Pd(PPh_3)$_2$][BF_4] in DMF exhibited one thin singlet at $\delta_3 = 24.08$ (Figure 2b). After addition of one equivalent of nBu$_4$NOAc and two equivalents of dba to [(η^3-C_3H_5)Pd(PPh_3)$_2$][BF_4], the signal δ_3 became broad, while a set of two signals appeared at $\delta_1 = 27.35$ and $\delta_2 = 25.52$ (Figure 2c) that are characteristic of Pd^0(dba)(PPh_3)$_2$.[11b] Thus, starting either from Pd(dba)$_2$, two equivalents of PPh_3 and CH_2=CH–CH_2–OAc, or from [(η^3-C_3H_5)Pd(PPh_3)$_2$][BF_4] with two equivalents of dba and one equivalent of AcO$^-$ resulted in similar ^{31}P NMR spectra (compare Figure 2a and 2c).

These ^{1}H and ^{31}P NMR experiments indicate that a palladium(0) complex is formed together with the allylic acetate by attack of the acetate ion on the cationic π-allylpalladium complex. The fact that the ^{1}H and ^{31}P NMR signals of the cationic π-allylpalladium complex were broad in the presence of dba and acetate ion evidences that this complex is involved in an equilibrium [see Eq. (8)].

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

Moreover, since broad and thin signals were simultaneously observed on the same NMR spectrum, the equilibrium shown in Equation (8) involves at least two successive equilibria with different equilibration rates. Thus, we tend to consider that (η^3-C_3H_5)Pd(PPh_3)$_2^+$ and AcO$^-$ are involved in a first and faster equilibrium than the second one, which connects the intermediate species formed to the final neutral species Pd^0(dba)(PPh_3)$_2$ and CH_2=CH–CH_2–OAc.

Evidence, by conductimetric studies in DMF, of the reversible formation of a cationic π-allylpalladium(II) complex in the oxidative addition of allylic acetate with the palladium(0) complex, which is formed in the mixture Pd(dba)$_2$ + 2 PPh$_3$: Since the oxidative addition of allylic acetate to a palladium(0) complex is supposed to produce ionic species, conductimetric experiments were performed in THF on a mixture of Pd^0(dba)$_2$ (2 mmol dm^{-3}) and two equivalents of PPh_3, after addition of 100 equivalents of CH_2=CH–CH_2–OAc. However, no significant conductance could be obtained at 20 °C. The resulting ionic π-allylpalladium(II) complex {(η^3-C_3H_5)Pd(PPh_3)$_2^+$AcO$^-$} is probably ion-paired in THF,[12] thus excluding any kinetic investigation by conductance measurements. Therefore, another solvent was investigated (DMF) in which free ions might be produced.

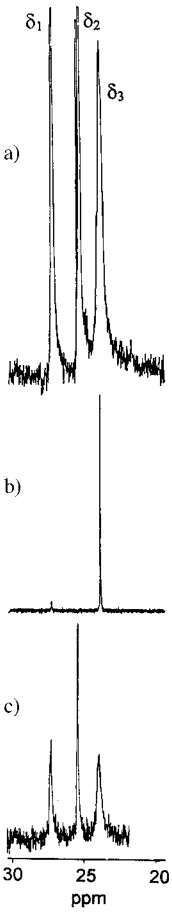


Figure 2. ^{31}P NMR spectrum (101 MHz) performed in 0.5 mL of DMF and 0.05 mL of [D$_6$]acetone with H_3PO_4 as an external reference. a) Pd(dba)$_2$, 2 equiv of PPh_3, and 50 equiv of CH_2=CH–CH_2–OAc. b) [(η^3-C_3H_5)Pd(PPh_3)$_2$][BF_4]. c) [(η^3-C_3H_5)Pd(PPh_3)$_2$][BF_4], 2 equiv of dba, and 1 equiv of nBu$_4$NOAc.

Conductimetric studies on a mixture of Pd^0(dba)$_2$ (2 mmol dm^{-3}) and two equivalents of PPh_3, in DMF at 20 °C, showed a residual conductance of 0.2 µS. After addition of $n = 6.2$ equivalents of CH_2=CH–CH_2–OAc, the conductance increased as a function of time to reach a plateau (Figure 3a). Successive addition of the allylic acetate resulted in the same phenomenon and enhanced the plateau conductance value (Figure 3a).

From these experiments one deduces qualitatively that on the one hand, ionic species are formed by the reaction of palladium(0) complex with the allylic acetate, and on the other hand that these ionic species are involved in an equilibrium with the starting reagents, because their concentration increases upon increasing the excess concentration of allylic acetate. Addition of increasing amounts of the allylic acetate resulted in a shift of the equilibrium towards the formation of the ionic species.

Figure 3b exhibits the variation of the conductivity of a solution of Pd(dba)$_2$ (2 mmol dm^{-3}), containing two equivalents of PPh_3 and fifty equivalents of the allylic acetate, in the presence of increasing amounts of dba, in DMF at 2 °C. When

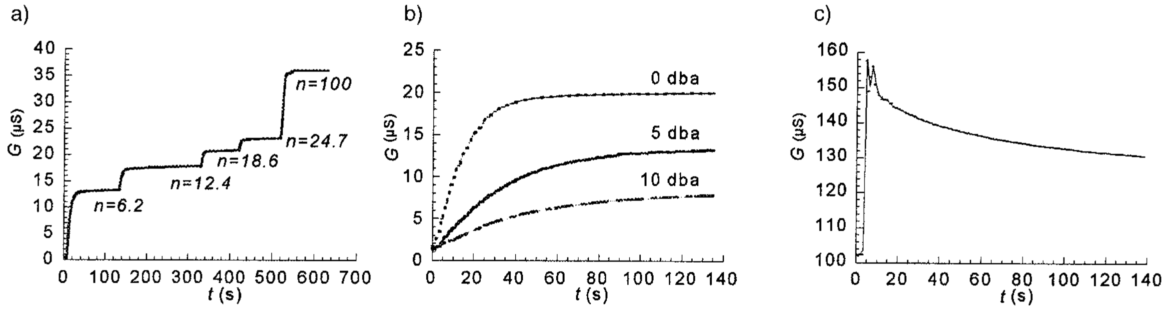


Figure 3. Conductance measurements in DMF. a) $Pd(dba)_2$ (2 mmol dm^{-3}) and PPh_3 (4 mmol dm^{-3}) in the presence of n equiv of $CH_2{=}CH{-}CH_2{-}OAc$ at 20 °C. b) $Pd(dba)_2$ (2 mmol dm^{-3}), PPh_3 (4 mmol dm^{-3}), and $CH_2{=}CH{-}CH_2{-}OAc$ (100 mmol dm^{-3}) in the presence of various amounts of dba at 2 °C. c) $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ (2 mmol dm^{-3}) alone and then addition of 2 equiv of dba and 1 equiv of nBu$_4$NOAc at 20 °C.

the concentration of dba increased, the limiting value of the conductance of the solution decreased; this shows that dba also controls the equilibrium concentration of the ionic species, whose concentrations decreased when the concentration of dba increased.

Therefore, Equation (9) reasonably expresses the overall equilibrium taking place when the allylic acetate is added to a solution of $Pd^O(dba)_2$ and two equivalents of PPh_3 (note that the formation of $Pd^O(dba)(PPh_3)_2$ is omitted for clarity [see Eq. (5)][10a]). The complex $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+[AcO]^-$ could formally be synthesized in situ by mixing stoichiometric amount of $[n\text{Bu}_4N]^+[AcO]^-$ and $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+[BF_4]^-$ according to Equation (10).

$$Pd^O(dba)(PPh_3)_2 + CH_2{=}CH{-}CH_2{-}OAc \xrightleftharpoons{K_0} (\eta^3\text{-}C_3H_5)Pd(PPh_3)_2^+ + OAc^- + dba \qquad (9)$$

$$[n\text{Bu}_4N]^+[AcO]^- + [(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+[BF_4]^- \longrightarrow [(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+[AcO]^- + [n\text{Bu}_4N]^+[BF_4]^- \qquad (10)$$

The conductance of a solution of nBu$_4$NOAc (2 mmol dm^{-3}) in DMF at 20 °C, was $G_1 = 89$ μS. The conductance of a solution of the ionic complex $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ (2 mmol dm^{-3}) was $G_2 = 96.5$ μS. The conductance of a solution of $[n\text{Bu}_4N][BF_4]$ (2 mmol dm^{-3}) was $G_3 = 136.5$ μS. For these three salts, the conductivity varied linearly with their concentration (in the range used here, i.e., from 0.2 to 6 mmol dm^{-3}) demonstrating that free anions and cations were present in solution without significant involvement of ions pairs. If the reaction given in Equation (10) were quantitative, the conductance of the complex $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+[AcO]^-$ should be $G_4 = (G_1 + G_2) - G_3 = 49 \pm 3$ μS. As shown in Figure 3a, this limiting value was not reached even in the presence of 100 equivalents of allylic acetate (36 μS), showing that the formation of the complex $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+[AcO]^-$ is not quantitative. This may be a result of an involvement in the equilibrium shown in Equation (9), which could not be totally shifted to its right-hand side and/or because the π-allylpalladium(II) complex formed in Equation (9) was partially ion-paired.

The reaction of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ with AcO^- and dba was also monitored by conductivity in DMF. The conductivity of a solution of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+[BF_4]^-$ (2 mmol dm^{-3}) increased rapidly after addition of two equivalents of dba and one equivalent of nBu$_4$NOAc; this is a result of the additional conductivity of nBu$_4$NOAc (Figure 3c). However, within a few seconds we observed a decay of the conductivity of the solution indicating that ionic species were consumed and that neutral species were slowly formed as a function of time. This experiment demonstrates that the acetate ions are able to react with a cationic π-allylpalladium(II) complex to form neutral species [Eq. (8)].[13] This is the first quantitative evidence in favor of the reversibility established qualitatively in Equation (9).

Further evidence of the reversibility of the oxidative addition of allylic acetate with the palladium(0) complex formed in the mixture $Pd(dba)_2 + 2\,PPh_3$

By UV spectroscopy: determination of the equilibrium constant in DMF and THF: As already reported, the complex $Pd(dba)(PPh_3)_2$ (1 mmol dm^{-3} in DMF), quantitatively formed in mixture of $Pd(dba)_2 + 2\,PPh_3$, was characterized by UV spectroscopy with its absorption band at $\lambda_{max} = 396$ nm (Figure 4a).[10b] Addition of six equivalents of $CH_2{=}CH{-}CH_2{-}OAc$ to this solution resulted in a fast decay of the absorbance of $Pd(dba)(PPh_3)_2$ which quickly reached a constant value. Successive additions of excess of the allylic acetate resulted in successive additional decays of the absorbance of $Pd(dba)(PPh_3)_2$, showing that the concentra-

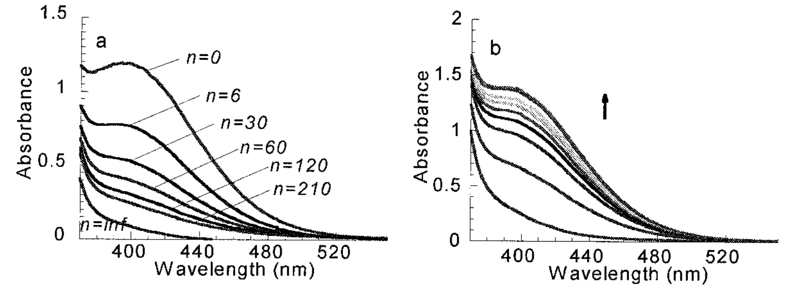


Figure 4. UV spectrum performed in DMF in a 1 mm path cell. a) $Pd(dba)_2$ (1 mmol dm^{-3}) and PPh_3 (2 mmol dm^{-3}) in the presence of n equiv of $CH_2{=}CH{-}CH_2{-}OAc$ at 20 °C. b) $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ (2 mmol dm^{-3}), dba (4 mmol dm^{-3}), and nBu$_4$NOAc (2 mmol dm^{-3}) at 20 °C as a function of time (Δt = 6.5 s between two spectra).

tion of this complex was controlled by an equilibrium involving the allylic acetate. We deduce from Figure 4a that more than 210 equivalents of allylic acetate were required to drive the reaction to completion, as evidenced by the complete disappearance of the $Pd(dba)(PPh_3)_2$ absorption band. The decay of the absorbance of $Pd(dba)(PPh_3)_2$ at $\lambda_{max} = 396$ nm was concomitant with the increase of the absorbance of dba, at $\lambda_{max} = 330$ nm. At least three isobestic points were observed, characterizing species involved in an equilibrium as described in Equation (9).

The reaction of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ with two equivalents of dba and one equivalent of AcO^- was monitored by UV spectroscopy in DMF (Figure 4b). A solution of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ (2 mmol dm^{-3}) did not exhibit any absorbance bands at around 400 nm. After addition of two equivalents of dba and one equivalent of $n\text{Bu}_4\text{NOAc}$, the absorption band characteristic of $Pd(dba)(PPh_3)_2$ at $\lambda_{max} = 396$ nm grew as a function of time (Figure 4b). This experiment definitively establishes that the acetate ions react with the cationic π-allylpalladium(II) complex to regenerate a palladium(0) complex as in Equation (8).

We conclude that the oxidative addition of the allylic acetate with the palladium(0) complex formed in situ from a mixture of $Pd(dba)_2 + 2\,PPh_3$ is a reversible reaction leading to a cationic π-allylpalladium(II) complex and one acetate ion. The equilibrium constant K_0 has been calculated in DMF based on the UV spectra of solutions of $Pd(dba)_2$ containing two equivalents of PPh_3 and various amounts of $CH_2{=}CH{-}CH_2{-}OAc$. In a first attempt, we only considered the formation of free ions in solution [see Eq. (9)].

At equilibrium $[Pd(dba)L_2] = C_0(1-x)$, $[CH_2{=}CH{-}CH_2{-}OAc] = C_0(n-x)$, $[\eta^3\text{-}C_3H_5)PdL_2^+] = [OAc^-] = C_0x$, and $[dba] = C_0(1+x)$, in which C_0 is the initial concentration of $Pd(dba)_2$, n is the number of equivalents of the allylic acetate and $x = (D_0 - D_{eq})/(D_0 - D_\infty)$ (D_0: initial absorbance of $Pd^0(dba)(PPh_3)_2$, D_{eq}: absorbance at the equilibrium position, D_∞: absorbance when the equilibrium in Equation (9) is totally shifted to its right-hand side). D values were measured at $\lambda = 405$ nm.[14] The equilibrium constant K_0 is therefore given by Equation (11).

$$K_0 = \frac{[\eta^3\text{-}C_3H_5)PdL_2^+][OAc^-][dba]}{[Pd(dba)L_2][CH_2{=}CH{-}CH_2{-}OAc]} = \frac{C_0x^2(1+x)}{(1-x)(n-x)}$$

$$\frac{K_0}{C_0} = \frac{x^2(1+x)}{(1-x)(n-x)} \qquad (11)$$

The plot of $C_0(1+x)/(n-x)(1-x)$ *versus* $1/x^2$ for different values of n and C_0, gives a straight line with a zero intercept (Figure 5), thus confirming that ion-pairing is negligible. The equilibrium constant is then readily calculated from the slope, $K_0(\text{DMF}) = 3.5(\pm 0.4) \times 10^{-5}$ mol dm^{-3}, at 20 °C.

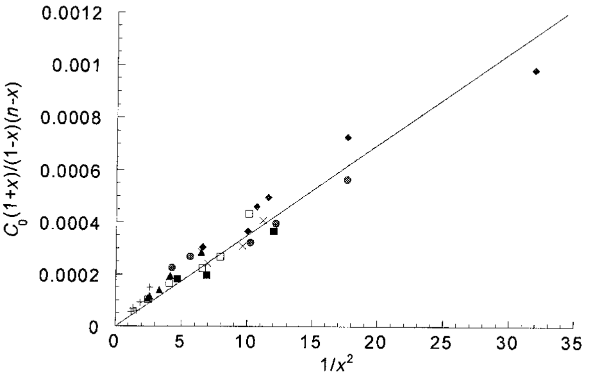


Figure 5. Determination of the equilibrium constant K_0 in DMF [Eq. (9)] from UV spectroscopy. Plot of $C_0(1+x)/(1-x)(n-x)$ as a function of $1/x^2$. $C_0 = [Pd(dba)_2]_0$, n equiv of $CH_2{=}CH{-}CH_2{-}OAc$, $x = (D_0 - D_{eq})/(D_0 - D_\infty)$ (D_0: initial absorbance of $Pd^0(dba)(PPh_3)_2$, D_{eq}: absorbance at the equilibrium position, D_∞: absorbance when the equilibrium [Eq. (9)] is totally shifted to its right-hand side). Slope $= 3.5 \times 10^{-5}$ M, $\rho = 0.97$.

From the above value of K_0, one can evaluate x for any values of n and C_0. The conductance measured for different values of n (from the plateaus of Figure 3a) can then be plotted as a function of x. This plot represented in Figure 6a is a straight line extrapolated to $x = 1$. This extrapolated conductance value of 56 ± 3 µS corresponds to the quantitative formation of $(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2^+$ and AcO^- in Equation (9), under the experimental conditions of Figure 3a. This extrapolated value is close to the theoretical value of 49 µS, calculated above for free ions [Eq. 10]. This again supports the fact that $(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2^+$ and AcO^- are formed as free ions in DMF through the reaction in Equation (9), therefore validating *a posteriori* the hypothesis we used for the calculation of K_0. The extrapolated value of the conductance was determined for different concentrations C_0 of $Pd(dba)_2$ and plotted as a function of C_0 (in the range of 1 to 10 mmol dm^{-3}). Figure 6b shows that the conductance of cationic complex/acetate ion solutions varied linearly with the palladium concentration. This definitively establishes that there are free ions in DMF and no significant ion pairing.

In THF, the complex $Pd(dba)(PPh_3)_2$, (1 mmol dm^{-3}) quantitatively formed in the mixture of $Pd(dba)_2$ and two equivalents of PPh_3 exhibited an adsorption band at $\lambda_{max} = 394$ nm. Successive additions of $CH_2{=}CH{-}CH_2{-}OAc$ resulted in a decay of the absorbance, which reached a constant value. As in DMF, the oxidative addition is a reversible reaction.

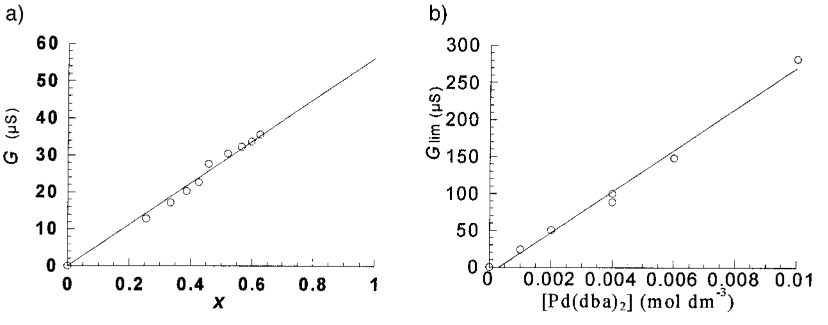


Figure 6. a) Plot of the conductance of solutions of $Pd(dba)_2$ (2 mmol dm^{-3}), PPh_3 (4 mmol dm^{-3}), and n equiv of $CH_2{=}CH{-}CH_2{-}OAc$ (from the plateaus of Figure 3a) versus x (calculated from the experimental value of K_0) at 20 °C. $\rho = 0.995$. **b)** Plot of the conductance (calculated by extrapolation to $x = 1$ as in Figure 6a) versus the concentration of $Pd(dba)_2$ at 20 °C. $\rho = 0.994$.

Since the π-allylpalladium(II) complex $\{(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2^+,AcO^-\}$ was found to be ion-paired in THF, the expression of the equilibrium constant [Eq. (13)] for the reaction given in Equation (12) differs from that expressed in DMF, in which only ion pairs are considered [see above Eqs. (9) and (11)].

$$Pd^O(dba)(PPh_3)_2 + CH_2{=}CH{-}CH_2{-}OAc \overset{K_0^*}{\rightleftharpoons} \{(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2^+,OAc^-\} + dba \qquad (12)$$

$$K_0^* = \frac{[\{\eta^3\text{-}C_3H_5)PdL_2^+OAc^-\}][dba]}{[Pd(dba)L_2][CH_2{=}CH{-}CH_2{-}OAc]} \qquad (13)$$

$$K_{00}^* = \frac{x(1\ +\ x)}{(1-x)(n-x)}$$

At equilibrium $[Pd(dba)L_2] = C_0(1-x)$, $[CH_2{=}CH{-}CH_2{-}OAc] = C_0(n-x)$, $[\{\eta^3\text{-}C_3H_5)PdL_2^+OAC^-\}] = C_0x$, and $[dba] = C_0(1+x)$, in which C_0 is the initial concentration of $Pd(dba)_2$, n the number of equiv of the allylic acetate and $x = (D_0 - D_{eq})/(D_0 - D_\infty)$ (D_0: initial absorbance of $Pd^O(dba)(PPh_3)_2$, D_{eq}: absorbance at the equilibrium position, D_∞: absorbance when the equilibrium [Eq. (12)] is totally shifted to its right-hand side). Absorbencies D were measured at $\lambda = 405$ nm and K_0 was calculated for different values of x and n. $K_0^*(THF) = 1\ (\pm 0.4) \times 10^{-2}$ at 20 °C.

By cyclic voltammetry: As already reported, voltammetry of a mixture of $Pd^O(dba)_2$ (2 mmol dm^{-3}) and two equivalents of PPh_3 performed at a rotating disk electrode in DMF, exhibits the two successive oxidation waves O_1, characteristic of $Pd^O(PPh_3)_2$, and O_2, characteristic of $Pd(dba)(PPh_3)_2$, involved in the equilibrium given in Equation (6).[10a] Addition of one equivalent of $CH_2{=}CH{-}CH_2{-}OAc$ resulted in an immediate, but small, decay of these oxidation waves (Figure 7a) and provoked a shift to less positive potentials. After successive additions of the allylic acetate, one observed corresponding decays of the oxidation currents to zero at large excesses of the allylic acetate. Since the current is proportional to the concentration of the palladium(0) complexes, we conclude again that the palladium(0) complexes are involved in an equilibrium with the allylic acetate as in given in Equation (9).

A third oxidation wave O_3 was also observed. Its oxidation current grew with the concentration of the allylic acetate, while those of waves O_1 and O_2 decayed. Wave O_3 was readily assigned to the oxidation of the acetate anions, by comparison with the voltammetry of authentic samples of nBu$_4$NOAc. In the presence of 200 equivalents of allylic acetate, the palladium(0) complexes almost disappear (Figure 7a) and the oxidation wave O_3 of the acetate ions was only observed.

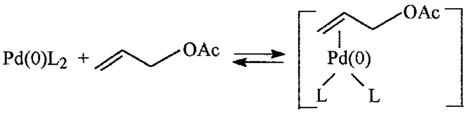
The cyclic voltammogram of a solution of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$, 2 mmol dm^{-3}, in DMF did not exhibit any oxidation peaks, but a main reduction peak R_0 was observed at −1.31 V versus SCE (Figure 7b). After addition of two equivalents of dba and one equivalent of nBu$_4$NOAc, the oxidation wave O_2, characteristic of $Pd(dba)(PPh_3)_2$, was observed at +0.55 V versus SCE.[10a] This experiment stresses again that the acetate ions react with the cationic π-allylpalladium(II) complex to regenerate a palladium(0) complex as given in Equation (8).

Conclusion

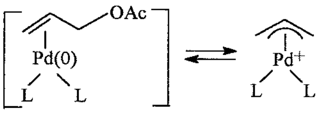
All these experiments establish that, in DMF, the oxidative addition of allylic acetate with the palladium(0) complex, generated from a mixture consisting of $Pd(dba)_2 + 2PPh_3$ [Eqs. (5) and (6)], affords cationic π-allylpalladium(II) complexes by a reversible process involving at least three successive equilibria [Eqs. (6), (14), and (15)], leading to an overall equilibrium situation in which no significant ion pairing occurs (Scheme 1).

$$Pd^0(dba)_2 + 2L \longrightarrow Pd^0(dba)L_2 \qquad (5)$$

$$Pd^0(dba)L_2 + S \rightleftharpoons SPd^0L_2 + dba \qquad (6)$$



(14)



(15)

The equilibrium shown in Equations (14) and (15) are connected through a common intermediate. Although not demonstrated in this work, the palladium(0) is probably ligated by the olefin double bond as it is in $Pd(dba)(PPh_3)_2$ complex.[10] In THF, the same reactions occur except that one must consider that, in addition, almost complete ion pairing occurs so that almost no free ions produced (Scheme 1).

Our work evidences that the role of the acetate ion cannot be considered as a simple inno-

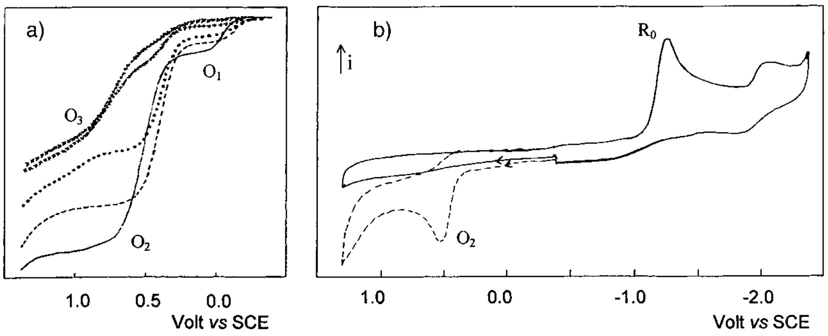
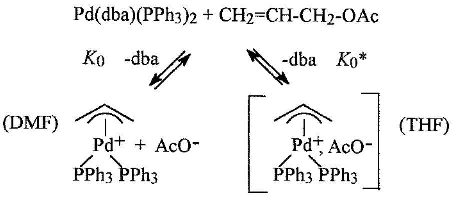


Figure 7. a) Cyclic voltammetry performed in DMF (containing nBu$_4$NBF$_4$, 0.3 mol dm^{-3}) at a rotating gold disk electrode (i. d. = 2 mm, scan rate of 20 mV s^{-1}, angular velocity of 105 rad s^{-1}) at 20 °C. $Pd(dba)_2$ (2 mmol dm^{-3}) and PPh_3 (4 mmol dm^{-3}) in the presence of: (—) 0, (- - -) 1, (· · ·) 5, (+ ++) 50, and (x x x) 200 equiv of $CH_2{=}CH{-}CH_2{-}OAc$ at 20 °C. b) Cyclic voltammetry performed in DMF (containing nBu$_4$NBF$_4$, 0.3 mol dm^{-3}) at a stationary gold disk electrode (i. d. = 0.5 mm, scan rate of 200 mV s^{-1}) at 20 °C: (—) $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ (2 mmol dm^{-3}); (- - -) $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ (2 mmol dm^{-3}), PPh_3 (4 mmol dm^{-3}), and nBu$_4$NOAc (2 mmol dm^{-3}).



Scheme 1. Overall equilibrium situation in DMF and THF. $K_0 = 3.5(\pm 0.4)\times 10^{-2}$ in DMF at 20°C; $K_0^* = 1(\pm 0.4)\times 10^{-2}$ in THF at 20°C.

cent leaving group. Indeed, its reaction as a nucleophile with the π-allylpalladium(II) complex can compete with other softer nucleophiles.[8] This competition of course becomes higher and higher as the reaction proceeds due to increasing concentration of acetate ions, released from the allylic acetate with concomitant decay of the nucleophile concentration. In DMF (free ions) the acetate ion is located far from the cationic π-allylpalladium(II) center and may not greatly influence the electronic density on the palladium(II) atom. On the other hand, in THF the acetate ion sticks on the palladium(II) complex (ions pair) and, consequently, not only diminishes the positive charge on the palladium(II), but also enhances/modifies the steric hindrance around the palladium; these two factors should influence the reactivity of the π-allylpalladium(II) complex with nucleophiles.

These results concerning the reversibility of the oxidative addition, that is, the existence of the backward reaction in Equation (15), are in agreement with work done by Trost and Bäckvall[7, 8] as recalled in the Introduction. Our work establishes this reversibility kinetically and determines the thermodynamics of the equilibrium. However, the exact mechanism (one or two steps) of the backward reaction in Equation (15) cannot be clarified from our work. Based on literature, two situations may occur as a function of the nucleophilic properties of the acetate. If the acetate anion is considered as a soft nucleophile, it gives rise to an *anti* attack with inversion of the configuration[15a] on the cationic π-allylpalladium complex (itself resulting from an *anti* oxidative addition with inversion of the configuration[15b]), and the overall reaction should lead to the initial enantiomer with retention of the configuration. The partial observed inversion is generally understood as an inversion of the stereochemistry of the π-allylpalladium(II) complex either by a π–σ–π mechanism[2a,f, 8a, 16] or by an S_N2 reaction of the palladium(0) complex with the π-allylpalladium(II) complex, as established by Bäckvall et al.[8d] The acetate ion may interfere in one of these two mechanisms. Moreover, a mechanism in which racemization would proceed by an internal attack of the allyl moiety by the acetate ligated to the palladium is not excluded.[8, 17] In the presence of a chiral ligand, the racemization of a prochiral allylic acetate as a consequence of a reversible oxidative addition should favor enantioselectivity by dynamic kinetic resolution.

When other allylic derivatives are considered, the oxidative addition may be not reversible as it will depend on the nucleophilic properties of the leaving group. In such cases, fast inversion of the intermediate diastereoisomeric π-allylpalladium(II) complexes is required to achieve enantioselectivity.[2a] The mechanism of oxidative addition of allylic acetates with palladium(0) complexes, generated in situ in mixtures of $Pd(dba)_2$ and phosphine ligands, is now under investigation as a function of the leaving group and the ligand in order to examine the generality of this reaction.

Experimental Section

General: ^{31}P NMR spectra were recorded on a Bruker spectrometer (101 MHz) with H_3PO_4 as an external 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 kept under argon. Commercial allylic acetate $CH_2{=}CH{-}CH_2{-}OAc$ (Acros) was used after filtration on alumina. Commercial π-allylpalladium(II) chloride dimer complex, $[\{Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$ (Acros), was used without any purification. $Pd(dba)_2$ was prepared according to described procedures.[18] The synthesis of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ was adapted from a related procedure.[4]

Synthesis of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$: PPh_3 (0.262 g, 1 mmol) in acetone (3 mL) was added to a solution of $[\{Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$ (0.1 g, 0.27 mmol) in acetone (5 mL). Water (4 mL) was added followed by $NaBF_4$ (0.161 g, 1.5 mmol) in water (2 mL), leading to the formation of a precipitate. Crystallization from dichloromethane/methanol afforded white crystals of pure $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$. The complex was characterized by ^1H and ^{31}P NMR spectroscopy (see Figures 1 and 2).

UV experiments: These experiments were performed in a thermostated 1 mm path-length cell on mixtures of $Pd(dba)_2$ (1 mmol dm^{-3}) and 2 equivalents of PPh_3 in DMF or THF and the suitable amount of $CH_2{=}CH{-}CH_2{-}OAc$. UV spectra of a solution of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ (2 mmol dm^{-3}) containing 2 equivalents of dba and 1 equivalent of nBu$_4$NOAc were recorded as a function of time.

Electrochemical set-up and electrochemical 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 about 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge filled with DMF (3 mL) containing nBu$_4$NBF$_4$ (0.3 mol dm^{-3}). DMF (12 mL) containing nBu$_4$NBF$_4$ (0.3 mol dm^{-3}) were poured into the cell followed by $Pd(dba)_2$ (13.8 mg, 0.024 mmol), PPh_3 (12.6 mg, 0.048 mmol), and various amounts of $CH_2{=}CH{-}CH_2{-}OAc$. Cyclic voltammetry was performed at a rotating gold disk electrode (i.d. 2 mm) with a scan rate of 20 mV s^{-1} and an angular velocity of 105 rad s^{-1}. Cyclic voltammetry was performed at a steady gold disk electrode (i.d. 0.5 mm) with a scan rate of 0.2 V s^{-1}) from a solution of $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2][BF_4]$ (18.2 mg, 0.024 mmol) in DMF, and then on the same solution containing dba (11.2 mg, 0.048 mmol) and nBu$_4$NOAc (7.2 mg, 0.024 mmol).

Acknowledgements

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