Oxidative Addition of Allylic Carbonates to Palladium(0) Complexes: Reversibility and Isomerization

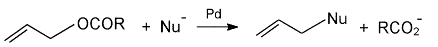
Christian Amatore,*[a] Sophie Gamez,[a] Anny Jutand,*[a] Gilbert Meyer,[a] Marcial Moreno-Mañas,*[b] Lurdes Morral,[b] and Roser Pleixats[b]

Abstract: The oxidative addition of a cyclic allylic carbonate to the palladium(0) complex generated from a [Pd(dba)$_2$]+2 PPh$_3$ mixture affords a cationic π-allylpalladium(II) complex with the alkyl carbonate as the counter-anion. This reaction is reversible and proceeds with isomerization of the allylic carbonate at the allylic position. The equilibrium constant has been determined in DMF. The influence of the precursor of the palladium(0) is discussed.

Keywords: allyl complexes · catalysts · oxidative addition · palladium

Introduction

Nucleophilic substitutions on allylic acetates [Eq. (1)][1] and carbonates [Eq. (2)][1, 2] are catalyzed by palladium(0) complexes (Tsuji–Trost reactions). Chiral ligands on the palladium induce enantioselective reactions.[3] Allylic carbonates have some advantages over allylic acetates. They are more reactive and do not require pre-formed anionic nucleophiles Nu$^-$. Instead, neutral pronucleophiles NuH can be used [Eq. (2)] since they may be deprotonated by the basic ethoxide RO$^-$ generated in situ by decarboxylation of the carbonate anion ROCO$_2^-$ which is released in the oxidative addition of the palladium(0) catalyst to the allylic carbonate.[1, 2]



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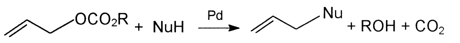

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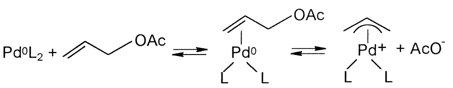
Kinetic investigations by us have demonstrated clearly that the first reaction of the catalytic cycle, namely the oxidative addition of palladium(0) complexes to *allylic acetates* is a reversible two-step reaction which leads to cationic π-allylpalladium(II) complexes. This has been established when the palladium ligand is PPh$_3$[4] [Eq. (3)] and for bidentate bisphosphine ligands (dppb, diop, dppf).[5]



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Starting from a cyclic allylic acetate and [Pd^0(PPh$_3$)$_4$], Trost et al.[6] have reported that the oxidative addition, in the absence of a nucleophile, proceeds with isomerization at the allylic position. This brought a clear evidence of the reversibility of the oxidative addition, a fact which could be responsible of the loss of stereospecificity in catalytic reactions. The isomerization process was first interpreted as an attack of the acetate ion, in which the acetate ion behaves as a nonstabilized nucleophile, on the cationic palladium(II) center followed by a reductive elimination (Scheme 1, route A).[6, 7] This route which requires a vacant site on the palladium(II) center is favored in the absence of any ligand and is inhibited by addition of chloride ions, as established by Bäckvall et al.[8] Later on, it was suggested that the isomerization might proceed via the equilibration of the intermediate π-allylpalladium(II) complex by a S$_N$2 mechanism induced by the palladium(0) complex (Scheme 1, route B), where the acetate anion behaves then as a stabilized nucleophile prone to attack the allyl ligand rather than the palladium(II) center.[9] Evidence of this S$_N$2 mechanism has been given by Bäckvall et al., starting from isolated cyclic cationic π-allylpalladium(II) complexes with BF$_4^-$ or TfO$^-$ as counter-anions.[10]

The oxidative addition of palladium(0) complexes to *allylic carbonates*, was generally regarded as a fast irreversible reaction due to the supposed fast decarboxylation of the carbonate anion ROCO$_2^-$ released in the reaction. In the absence of any nucleophile, palladium(0) complexes catalyze the formation of allylic ethers from allylic carbonates, the RO$^-$ anion formed by the decarboxylation of the alkyl carbonate anion acting as a nucleophile [Eq. (4)].[11]

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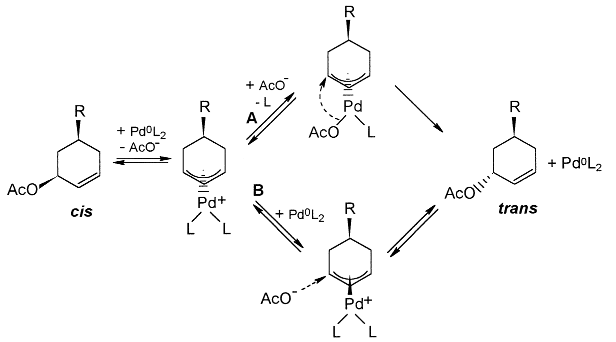
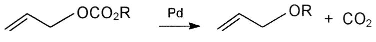


Scheme 1. Mechanisms of the palladium-catalyzed isomerization of allylic acetates.



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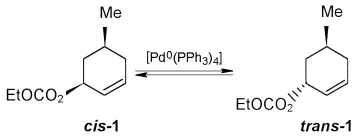
A loss of stereochemistry was observed when starting from a ***trans*** cyclic allylic carbonate. This was interpreted as resulting from partial isomerization of the starting allylic carbonate; this suggests that the oxidative addition was reversible and the decarboxylation of the alkyl carbonate anion not as fast.[11b] Indeed, some cationic π-allylpalladium(II) complexes have been synthesized by an oxidative addition of a palladium(0) complex to allylic carbonates by Ozawa and Yamamoto et al.[12] with the alkyl carbonate anion $ROCO_2^-$ as the counter-anion and PMe_3 as the ligand; this indicates that the decarboxylation of the alkyl carbonate anion is not so fast. Recently, stereochemical scrambling observed by us in palladium(0)-catalyzed allylation of anilines has been rationalized by considering a reversible oxidative addition which proceeds with isomerization of the starting allylic carbonate.[13] Isomerization was effectively observed in the presence of catalytic amount of $[Pd^0(PPh_3)_4]$ [Eq. (5)].

We report here kinetic results which confirm that the oxidative addition of palladium(0) complexes to allylic carbonates is indeed reversible and proceeds with isomerization of the starting allylic carbonate at the allylic position.

Abstract in French: *L'addition oxydante du carbonate allylique cyclique **1** avec le complexe du palladium(0), formé à partir d'un mélange: [Pd(dba)₂]+2PPh₃, conduit à un complexe π-allylpalladium(II) cationique avec le carbonate d'alkyle comme contre-anion. Cette réaction est réversible et elle s'accompagne d'une isomérisation au niveau du carbone allylique portant la fonction carbonate. La constante d'équilibre a été determinée dans le DMF. L'influence du précurseur du palladium(0) est discutée.*

Abstract in Spanish: *La adición oxidante entre el carbonato alílico cíclico **1** y el complejo de paladio(0) formado a partir de una mezcla: [Pd(dba)₂]+2PPh₃, conduce a un complejo catiónico de π-alilpaladio con el carbonato de alquilo como contraanión. Esta reacción es reversible y está acompañada de una isomerización en el carbono alílico que soporta la función carbonato. La constante de equilibrio ha sido determinada en DMF. La influencia del precursor de paladio(0) es discutida.*



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Results and Discussion

Among the various precursors of palladium(0) complexes used in allylic nucleophilic substitutions, mixtures of $[Pd^0(dba)_2]$ (dba = *trans,trans*-dibenzylidenacetone) and phosphine ligands, afford efficient catalysts.[1–3] The reversibility of the oxidative addition of the allylic acetate to the palladium(0) generated from $[Pd(dba)_2]+2\,PPh_3$ in DMF (*S*) has been kinetically established and the value of the overall equilibrium constant determined in the following Equations (6)–(9).[4]

$$[Pd^0(dba)_2] + 2\,PPh_3 \rightarrow [Pd^0(dba)(PPh_3)_2] + dba \qquad (6)$$

$$[Pd^0(dba)(PPh_3)_2] \rightleftarrows [Pd^0(PPh_3)_2] + dba \qquad (7)$$

$$[Pd^0(PPh_3)_2] + CH_2{=}CH\text{-}CH_2\text{-}OAc \rightleftarrows [(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+ + AcO^- \qquad (8)$$

overall equilibrium: $K_0/C_0 = 0.035$ (DMF, 20 °C):

$$[Pd^0(dba)(PPh_3)_2] + CH_2{=}CH\text{-}CH_2\text{-}OAc \overset{K_0}{\rightleftarrows} [(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+ + AcO^- + dba \qquad (9)$$

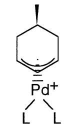
The oxidative addition performed under the same conditions with the allylic carbonate $CH_2{=}CH\text{-}CH_2\text{-}OCO_2Et$ resulted in a faster and irreversible reaction; the rate constant *k* was determined from conductivity measurements [Eq. (10)]:

$$[Pd^0(dba)(PPh_3)_2] + CH_2{=}CH\text{-}CH_2\text{-}OCO_2Et \xrightarrow{k} [(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+ + EtOCO_2^- + dba \qquad (10)$$

where $k = 1.5\ mol\,dm^{-3}\,s^{-1}$ (DMF, −15 °C).

After prolonged reaction times, the starting palladium(0) complex $[Pd^0(dba)(PPh_3)_2]$ was partially recovered together with some $CH_2{=}CH\text{-}CH_2\text{-}OEt$ [Eq. (4)], which indicates that some decarboxylation of the carbonate $EtOCO_2^-$ had occurred after a longer period of time.[11]

The allylic carbonate ***cis*-1**, which is expected to be less reactive than $CH_2{=}CH\text{-}CH_2\text{-}OCO_2Et$, was tested in its oxidative addition to the palladium(0) complex generated from $[Pd(dba)_2]+2\,PPh_3$. The oxidative addition is supposed to afford the cationic ***trans*-2** π-allylpalladium(II) complex in the first step.



***trans*-2**

Evidence of the reversible formation of a cationic π-allylpalladium(II) complex in the oxidative addition of the allylic carbonate *cis*-1 to the palladium(0) complex formed from [Pd(dba)₂+2PPh₃] by conductivity measurements in DMF

As for allylic acetates, the oxidative addition of allylic carbonates to palladium(0) complexes is supposed to produce ionic species, that is a cationic π-allylpalladium(II) complex with $EtOCO_2^-$ as the counter-anion.[12] Conductivity measurements have been performed in DMF at 20 °C with a solution of $[Pd^0(dba)_2]$ (2 mmol dm^{-3}) and two equivalents of PPh_3, in the presence of various amount of the allylic carbonate ***cis*-1** (Figure 1). Starting from a residual conductivity of 1 µS, after addition of $n = 1.8$ equiv ***cis*-1**, the conductivity increased as a function of time to reach a plateau (Figure 1, part a). Successive addition of ***cis*-1** resulted in the same phenomenon thus enhancing the plateau conductivity value. From these experiments, it is established that ionic species are indeed formed by reaction of a palladium(0) complex with the allylic carbonate and that this reaction is an equilibrium because the ionic species steady concentration increased when the allylic carbonate concentration is increased beyond the 1:1 stoichiometry. The conductivity decreased when dba was added (Figure 1, part b), establishing that dba is involved in the equilibrium with the allylic carbonate and shifts the equilibrium back to the formation of the neutral allylic carbonate. Since the anion $EtOCO_2^-$ has been characterized by ^{1}H-NMR spectroscopy (vide infra), we assume that the allylic carbonate ***cis*-1** reacts with the palladium(0) through an overall reversible reaction (11) which affords a cationic π-allylpalladium(II) complex **2** with $EtOCO_2^-$ as the counter-anion.

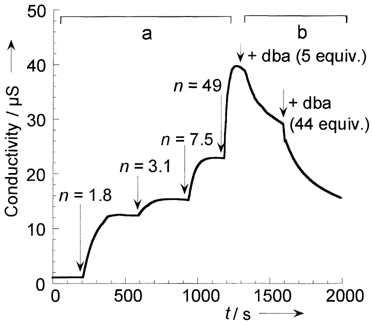


Figure 1. Conductivity measurements in DMF at 20 °C. Part a: $[Pd(dba)_2]$ (2 mmol dm^{-3}) and PPh_3 (4 mmol dm^{-3}) in the presence of n equivalents of ***cis*-1**. Part b: $[Pd(dba)_2]$ (2 mmol dm^{-3}), PPh_3 (4 mmol dm^{-3}), ***cis*-1** (98 mmol dm^{-3}) in the presence of added dba: 5 and then 44 equiv compared with $[Pd(dba)_2]$.

$$[Pd^0(dba)(PPh_3)_2] + \text{allyl-}OCO_2Et\ (\mathbf{1}) \overset{K_1}{\rightleftharpoons} [(\eta^3\text{-allyl})Pd(PPh_3)_2]^+\ (\mathbf{2}) + EtOCO_2^- + dba \qquad (11)$$

Evidence of the reversibility of the oxidative addition of the allylic carbonate *cis*-1 to the palladium(0) complex formed from [Pd(dba)₂]+2 PPh₃ by UV spectroscopy: Determination of the equilibrium constant in DMF

As already reported, the complex $[Pd^0(dba)(PPh_3)_2]$ (1 mmol dm^{-3} in DMF) formed in a $\{[Pd(dba)_2]+2\,PPh_3\}$ mixture[14a] is characterized by its absorption band ($\lambda_{max} = 396$ nm) in UV spectroscopy (Figure 2, left).[14b] Addition of one equivalent of ***cis*-1** to this solution resulted in a fast decay of the absorbance of $[Pd^0(dba)(PPh_3)_2]$ which reached a constant value. Successive additions beyond the 1:1 stoichiometry of ***cis*-1** resulted in successive additional decays of the absorbance of $[Pd^0(dba)(PPh_3)_2]$, thus confirming that this complex and ***cis*-1** are involved in an equilibrium (11). The equilibrium constant K_1 was determined from UV spectra of solutions of $[Pd(dba)_2]$ (initial concentration: C_0) containing two equivalents of PPh_3 and various amounts of ***cis*-1** (n equivalents).

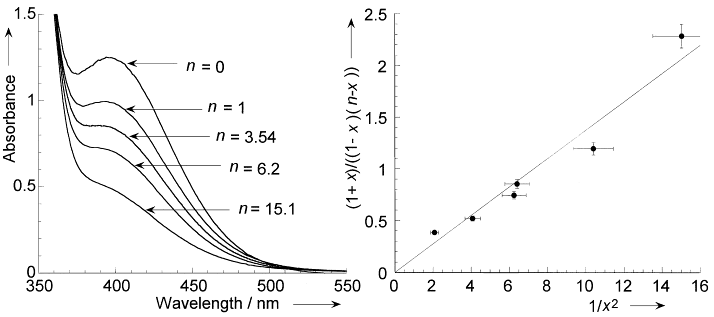


Figure 2. Left: UV spectrum performed in DMF in a 1 mm path cell with a solution of $[Pd(dba)_2]$ (1 mmol dm^{-3}) and PPh_3 (2 mmol dm^{-3}) in the presence of n equivalents ***cis*-1** at 20 °C. Right) Determination of the equilibrium constant K_1 in DMF [Eq. (11)] from UV spectroscopy. Plot of $(1+x)/((1-x)(n-x))$ as a function of $1/x^2$. $C_0 = [Pd(dba)_2]_0$, n: equivalent of ***cis*-1**, $x = (D_0 - D_{eq})/(D_0 - D_\infty)$ (D_0: initial absorbance of $[Pd^0(dba)(PPh_3)_2]$, D_{eq}: absorbance at the equilibrium position, D_∞: absorbance when the equilibrium (11) is totally shifted toward its right-hand side). Slope = $0.14 = K_1/C_0$.

At equilibrium: $[Pd^0(dba)(PPh_3)_2] = C_0(1-x)$; $[\mathbf{1}] = C_0(n-x)$; $[\mathbf{2}] = C_0x$; $[EtOCO_2^-] = C_0x$; $[dba] = C_0(1+x)$

$$K_1 = \frac{[\mathbf{2}]\,[EtOCO_2^-]\,[dba]}{[Pd^0(dba)L_2]} \qquad \frac{K_1}{C_0\,x^2} = \frac{(1+x)}{(1-n)(n-x)}$$

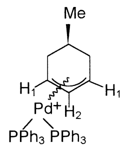
$x = (D_0 - D_{eq})/(D_0 - D_\infty)$ (D_0: initial absorbance of $[Pd^0(dba)(PPh_3)_2]$ at $\lambda = 420$ nm, D_{eq}: absorbance at the equilibrium position, D_∞: absorbance when the equilibrium (11) is totally shifted toward its right-hand side).

The plot of $(1+x)/((n-x)(1-x))$ versus $1/x^2$ for different values of n was linear with a zero intercept (Figure 2, right). The equilibrium constant K_1 was then determined from the slope of the regression line with $K_1/C_0 = 0.14\ (\pm\ 0.01)$ (DMF, 20 °C)

Evidence of the isomerization at the allylic position during the oxidative addition of allylic carbonate to [Pd⁰(PPh₃)₄] and to the palladium(0) complex formed from [Pd(dba)₂+2 PPh₃] by NMR spectroscopy

The isomerization of ***cis*-1** to ***trans*-1** has been already observed by us in the presence of a catalytic amount of $[Pd^0(PPh_3)_4]$ in THF at room temperature.[13] This reaction has been reinvestigated with $[Pd(dba)_2+2\,PPh_3]$ and a stoichiometric amount of ***cis*-1** to characterize the π-allylpalladium(II) complex **2** formed in the oxidative addition. The reaction was performed in $CDCl_3$ and monitored by ^{1}H-NMR spectroscopy (400 MHz). Twenty minutes after mixing, the spectrum showed the signals characteristic of the ***trans*-1** compound as identified by comparison with the authentic sample. Its concentration progressively increased as a function of time at the expense of **cis-1**. After 1 h, a ratio of ***cis*-1**:***trans*-1** 40:60 was found which is close to the equilibrium ratio observed when the isomerization was induced by $[Pd^0(PPh_3)_4]$.[13]

Additional signals were also observed twenty minutes after mixing, that is before the isomerization equilibrium ***cis*-1**/***trans*-1** was fully reached. A triplet at $\delta = 1.26$ (3H, $J = 7$ Hz) associated to two quadruplets at $\delta = 3.74$ and 3.75 (2H, $J = 7$ Hz) characterized for the CH_3 and CH_2 protons of the ethyl carbonate anion $CH_3CH_2OCO_2^-$.[12] A broad signal at $\delta = 4.93$ ($\Delta\nu_{1/2} = 60$ Hz) which integrated for 2H when compared with the signal of $CH_3CH_2OCO_2^-$ characterized the two allylic protons H_1 of the cationic π-allylpalladium(II) complex **2**.



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A second broad signal at $\delta = 6$ integrating for 1H characterized the allylic proton H_2 of complex **2**. These two signals are very similar in position to that of isolated related complexes[10] except that they are broader, as expected for species involved in an equilibrium. A thin doublet at $\delta = 0.99$ (3H, $J = 7$ Hz) characterized the Me substituent on the cycle in complex **2**. Due to the ***cis*-1/*trans*-1** isomerization process, the ***cis*-2** and ***trans*-2** complexes should be observed and characterized by two different doublets for the Me group as observed for OMe or CO_2Me substituents of related ***cis*** and ***trans*** cationic π-allylpalladium complexes.[10] A ^{31}P-NMR (101 MHz) spectroscopy performed on the same solution exhibited beside the two signals of $[Pd^0(dba)(PPh_3)_2]$ at $\delta = 26.81$ and 24.63, a signal at 23.11 assigned to the cationic π-allylpalladium complex **2**.[4] The ***cis*-2** and ***trans*-2** complexes could not be discriminated by ^{31}P- and ^{1}H-NMR performed in $CDCl_3$, thereby suggesting that they are involved in a fast equilibrium. However, in DMF, a solution of $[Pd(dba)_2]$ and $2\,PPh_3$ containing 6 equiv of ***cis*-1** exhibited, beside the two signals at $\delta = 27.47$ and 25.64 characteristic of $[Pd^0(dba)(PPh_3)_2]$, two broad signals at $\delta = 24.42$ ($\Delta\nu_{1/2} = 20$ Hz) and 23.58 ($\Delta\nu_{1/2} = 32$ Hz) in the ratio 38:62 which are assigned to both cationic complexes **2**.

These results show that the oxidative addition affords a cationic π-allylpalladium(II) complex with the ethyl carbonate as the counter-anion by an overall equilibrium [Eq. (12)] which is established in less than 20 min as observed in UV spectroscopy and by conductivity measurements while the overall ***cis*-1/*trans*-1** isomerization requires a much longer time. The ^{1}H-NMR signals of the cationic complex and of the ethyl carbonate anion in $CDCl_3$ remained unchanged after 1 h; this indicates a relative stability of the ethyl carbonate anion in chloroform[12] with respect to its decarboxylation.

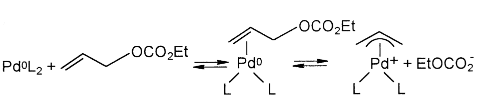
$$[Pd^0(dba)(PPh_3)_2] + \textbf{\textit{cis}-1/\textit{trans}-1} \rightleftharpoons \textbf{\textit{cis}-2/\textit{trans}-2} + EtOCO_2^- + dba \qquad K_1 \tag{12}$$

On the ^{1}H-NMR spectrum of a solution of $[Pd^0(PPh_3)_4]$ and one equivalent of ***cis*-1** in $CDCl_3$, a mixture of ***cis*-1** and ***trans*-1** was observed whose equilibrium ratio was already reached after 15 min. The ratio of the carbonate anion over the ***cis*-1** and ***trans*-1** mixture was about 20% higher than that obtained when the oxidative addition was performed from $[Pd(dba)_2]$+$2\,PPh_3$]; this gives evidence that the equilibrium (13) is more shifted toward its right-hand side than the equilibrium (12) (for example $K_2 > K_1$). However, the signal of the CH_2 protons of the ethyl carbonate anion was less resolved and appeared as one broad quadruplet instead of two quadruplets; this indicates that the equilibrium (13) is faster than (12) on the NMR time scale.

$$[Pd^0(PPh_3)_3] + \textbf{\textit{cis}-1/\textit{trans}-1} \rightleftharpoons \textbf{\textit{cis}-2/\textit{trans}-2} + EtOCO_2^- + PPh_3 \qquad K_2 \tag{13}$$

In DMF, a solution of $[Pd(PPh_3)_4]$ containing 30 equiv ***cis*-1** exhibited two broad signals at $\delta = 24.35$ ($\Delta\nu_{1/2} = 50$ Hz) and 23.50 ($\Delta\nu_{1/2} = 60$ Hz) in the ratio 42:58 which are assigned to both the cationic complexes **2**. These signals are broader than when starting from $[Pd(dba)_2]$+$2\,PPh_3$ (vide supra), which suggets that the complexes are involved in a faster equilibrium as observed in ^{1}H-NMR spectroscopy (vide supra).

Whatever the precursor of the palladium(0) complex, {$[Pd(dba)_2]$+$2\,PPh_3$} or $[Pd^0(PPh_3)_4]$, $[Pd^0(PPh_3)_2]$ is the active complex which reacts with the allylic carbonate [Eq. (14)].



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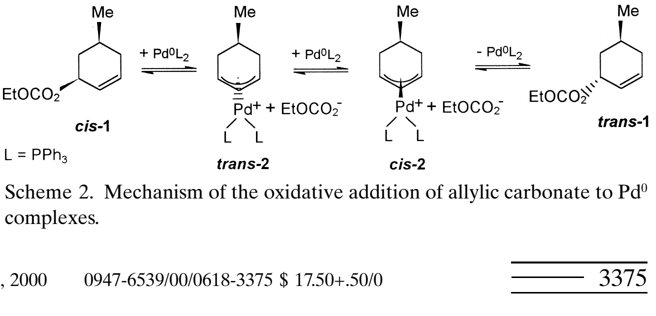
The main difference between the two catalytic precursors considered in this study stems from the availability of $[Pd^0(PPh_3)_2]$ whose concentration is controlled by equilibrium (15) or (16) according to the precursor.

$$[Pd^0(dba)(PPh_3)_2] \rightleftharpoons [Pd^0(PPh_3)_2] + dba \tag{15}$$

$$[Pd^0(PPh_3)_2] \rightleftharpoons [Pd^0(PPh_3)_2] + PPh_3 \tag{16}$$

From previous work[14a] it is known that the concentration of $[Pd^0(PPh_3)_2]$ in the equilibrium (16) is higher than in the equilibrium (15) and is responsible for the higher reactivity of $[Pd^0(PPh_3)_4]$ compared with that of {$[Pd(dba)_2]$+$2\,PPh_3$} in oxidative addition (about tenfold). The fact that the overall equilibrium (13) is slightly more shifted toward the formation of the cationic complex than the equilibrium (12) ($K_2 > K_1$) is then consistent with the overall higher reactivity of $[Pd^0(PPh_3)_4]$ compared with that of {$[Pd(dba)_2]$+$2\,PPh_3$} in oxidative addition. The higher concentration of $[Pd^0(PPh_3)_2]$ in equilibrium (16) versus that in equilibrium (15) is at the origin of the faster ***cis*-1/*trans*-1** equilibration observed when starting from $[Pd^0(PPh_3)_4]$. This is in favor of an overall isomerization proceeding through a reversible S_N2 mechanism between the ***trans*-2** and ***cis*-2** cationic complexes (Scheme 2), followed by the nucleophilic attack of the ethyl carbonate anion onto the π-allyl ligand.



Scheme 2. Mechanism of the oxidative addition of allylic carbonate to Pd^0 complexes.

As for [Pd(dba)$_2$]+dppe,[13] we did not observe any ***cis*-1**/***trans*-1** equilibration at room temperature when starting from [Pd(dba)$_2$]+(+)diop.

Conclusion

The oxidative addition of the allylic carbonate **1** to the palladium(0) complex generated from [Pd(dba)$_2$] and 2 PPh$_3$ affords a cationic π-allylpalladium(II) complex **2** with the ethyl carbonate as the counter-anion. The reaction is reversible ($K_1/C_0 = 0.14$ in DMF at 20 °C) and proceeds with isomerization at the allylic position. The isomerization rate depends on the precursor of the palladium(0) active in the oxidative addition.

Experimental Section

General: ^{1}H-NMR spectra were recorded on a Bruker spectrometer (400 MHz) with TMS as an internal reference. ^{31}P-NMR spectra were recorded on a Bruker spectrometer (101 MHz) with H$_3$PO$_4$ as an external reference. UV spectra were recorded on a DU 7400 Beckman spectrophotometer. Conductances were measured on a Tacussel CDM210 conductimeter (cell constant = 1 cm^{-1}).

Chemicals: DMF was distilled from calcium hydride under vacuum and kept under argon. PPh$_3$ was commercially available (Acros). [Pd(dba)$_2$][15] and ***cis*-1**[16] and were prepared according to reported procedures.

UV experiments: They were performed in a thermostated 1 mm path length cell on mixtures of [Pd(dba)$_2$] (1 mmol dm^{-3}) and 2 equiv PPh$_3$ in DMF and the suitable amount of the allylic carbonate ***cis*-1**.

Conductivity measurements: They were performed in a thermostated cell containing DMF (15 mL), [Pd(dba)$_2$] (17.2 mg, 0.03 mmol), PPh$_3$ (15.7 mg, 0.06 mmol), and the suitable amount of the allylic carbonate ***cis*-1**.

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