

Effect of the leaving group and the allylic structure on the kinetics and thermodynamics of the reaction of allylic carboxylates with palladium(0) complexes

Nicolas Agenet, Christian Amatore,* Sophie Gamez, Hadia Gérardin,
Anny Jutand,* Gilbert Meyer, and Céline Orthwein

*Ecole Normale Supérieure, Département de Chimie, UMR CNRS 8640, "PASTEUR"
24 Rue Lhomond, F-75231 Paris, Cedex 5, France
E-mail: christian.amatore@ens.fr; Anny.Jutand@ens.fr*

Dedicated to Professor M. Moreno-Mañas on the occasion of his 60th birthday
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Abstract

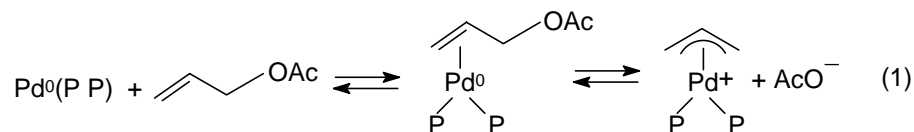
The reaction of allylic carboxylates (allyl-OZ, OZ: acetate, chloroacetate, trifluoroacetate, substituted benzoates, carbonate) with Pd⁰ complexes ligated by monodentate (PPh₃) or bidentate (dppb, dppf) ligands is a reversible multistep reaction, which eventually gives in DMF a cationic (η^3 -allyl)Pd^{II}(P P)⁺ complex with ZO⁻ as the counter anion (free ions). The formation of an intermediate neutral complex (η^2 -allyl-OZ)Pd⁰(P P) where the Pd⁰ is ligated to the C=C bond of the allylic carboxylate (complexation step) has been evidenced kinetically in the case of moderate OZ leaving groups (acetate, benzoates) for monodentate and bidentate phosphine ligands. The overall equilibrium constants and the rate constants of the complexation and oxidative addition-ionization steps (when not too fast) have been determined in DMF. With very good leaving groups (carbonate, trifluoroacetate), the oxidative addition-ionization step is faster than the complexation step whereas the oxidative addition-ionization step is the slowest step for less good leaving groups (acetate, benzoate). The forward rate constant of the equilibrium in which the active Pd⁰(PPh₃)₂ is formed from Pd⁰(dba)(PPh₃)₂ has been determined.

Keywords: Allylic carboxylate reactions, palladium(0) complexes, kinetics

Introduction

We have previously established that the reaction of the allyl *acetate* with Pd⁰(P P) complexes (first step of the Tsuji-Trost reactions)¹ is reversible (P P represents either 2PPh₃ or one bidentate bisphosphine ligand: dppf (1,1'-bis(diphenylphosphino)ferrocene), dppb (1,4-bis(diphenyl)phosphinobutane)).²⁻⁴ The reaction proceeds in two successive steps: reversible

complexation followed by a reversible oxidative addition (also called ionization step) (Eq. 1). The intermediate Pd⁰ complex ligated by the C=C bond of the allyl acetate has been kinetically evidenced when the Pd⁰ is ligated by bidentate bisphosphine ligands (dppb or dppf).³



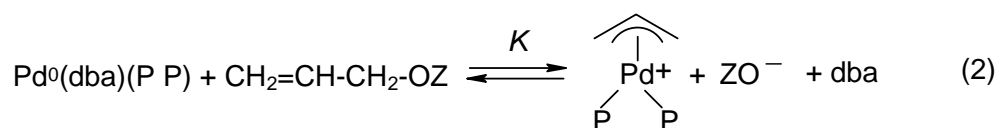
The reversibility of the reaction of a cyclic allylic *carbonate* has also been established with PPh₃ as well as an epimerization at the allylic position.⁵ Consequently, in a palladium-catalyzed nucleophilic allylic substitution, the acetate or carbonate ions whose concentration increases as the catalytic reaction proceeds, may compete with poor or stabilized nucleophiles in the nucleophilic attack on cationic (η^3 -allyl)palladium(II) complexes, leading thus to scrambling in the allylic substrates.^{5,6} This shows that acetate or carbonate ions are not only simple leaving groups as generally postulated, but that they may play an active role in the catalytic process.⁶

We report therein the effect of the leaving group and the structure of the allylic group on the kinetics and thermodynamics of the reaction of allylic carboxylates with palladium(0) complexes.

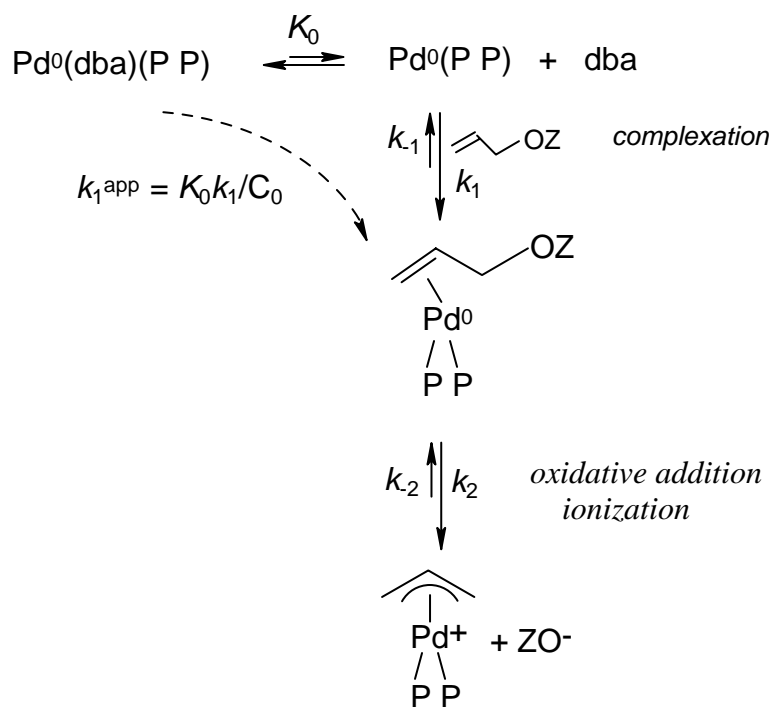
Results and Discussion

All reactions were performed in DMF starting from either Pd⁰(dba)₂ (C₀ = 1 mM) (dba = *trans,trans*-dibenzylideneacetone) and 2 equiv. PPh₃, i.e., from the complex Pd⁰(dba)(PPh₃)₂⁷ or from Pd⁰(dba)₂ and 1 equiv. of a bisphosphine ligand (P,P), i.e., from the complex Pd⁰(dba)(P,P) (P,P = dppf, dppb).⁸

The equilibrium constant *K* of the overall equilibrium (2) was determined by UV spectroscopy, which provides the concentration of Pd⁰(dba)(P,P) in the equilibrium² or by conductivity measurements, which provide the concentration of the cationic (η^3 -allyl)Pd(P,P)⁺ complex in the equilibrium³ (free ions in DMF), as previously reported for the simple allyl acetate CH₂=CH-CH₂-OAc.



This overall equilibrium (2) is the result of three successive equilibria (Scheme 1).

**Scheme 1**

Reaction of an allyl carboxylate with $\text{Pd}^0(\text{dba})(\text{P P})$ in DMF (PP represents either 2PPh_3 or one bidentate P,P ligand)

With a large excess of the allylic carboxylate or with a very reactive allylic carboxylate, the reaction (2) may be irreversible. The apparent rate constant $k_1^{\text{app}} = K_0 k_1 / C_0$ of the overall complexation step^[3] (Scheme 1) was then determined from UV kinetic data. The rate of formation of the cationic complex $(\eta^3\text{-allyl})\text{Pd}(\text{P P})^+$ was monitored by conductivity measurements. The rate constant, k_2 (Scheme 1) was determined when the ionization step was rate determining.^[3]

Kinetics and thermodynamics of the reaction of allyl carboxylates with Pd^0 complexes as a function of the leaving group

With PPh_3 as the ligand (Table 1, entries 1-12), one observes that the reaction of allyl carboxylates $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OZ}$ (Eq 2) is irreversible when considering very good OZ leaving groups such as carbonate and trifluoroacetate (Table 1, entries 1-4). The reversibility of the reaction could not be evidenced, even in the presence of a large excess of dba or PPh_3 or at low temperatures. The rate constants of the chemical steps (k_1^{app} and k_2 , Scheme 1) were too fast to be determined at 20 °C. This was achieved at lower temperatures (Table 1, entries 2,3) for the rate constant of the complexation step, k_1^{app} . For the $-\text{OCOCF}_3$ leaving group, the kinetic curve of the formation of the cationic complex was strictly exponential (no S-shaped) with a rate of formation equal to the rate of disappearance of $\text{Pd}^0(\text{dba})(\text{PPh}_3)_2$. This establishes that the rate of the oxidative addition-ionization step from the intermediate complex

$(\eta^2\text{-CH}_2=\text{CH-CH}_2\text{-OCOCF}_3)\text{Pd}^0(\text{P P})$ is faster than its rate of formation, which is then rate determining: $k_1^{\text{app}}[\text{CH}_2=\text{CH-CH}_2\text{-OCOCF}_3] < k_2$ (see last paragraph for the detailed mechanistic investigation of this reaction).

The reaction (2) is an equilibrium for less good leaving groups such as chloromethylacetate, benzoates and acetate (Table 1, entries 5-12). As expected, the determination of the equilibrium constants shows that the better the leaving group, the higher the equilibrium constant. In the benzoates series (Table 1, entries 6-11), the substitution of the phenyl group by an electron withdrawing group, which exalts the leaving group properties, favors the formation of the cationic complex $(\eta^3\text{-allyl})\text{Pd}(\text{P P})^+$. All these data are consistent with the effect of the leaving group. A good leaving group will favor the two forward reactions: the complexation step because the C=C double bond becomes less electron rich, and the oxidative addition step in which the leaving group is released. A good leaving group is also a poor nucleophile for the backward reaction of the last step (rate constant k_2). Consequently as expected, the better the leaving group, the higher the equilibrium constant and the higher the concentration of the cationic complex $(\eta^3\text{-allyl})\text{Pd}(\text{P P})^+$. In the benzoate series ($\text{CH}_2=\text{CH-CH}_2\text{-OBz}$), the rate constants k_1^{app} and k_2 were determined at 10 °C. The kinetic curves for the formation of the cationic complexes were all S-shaped. This is an evidence for the formation of the intermediate complex $(\eta^2\text{-CH}_2=\text{CH-CH}_2\text{-OBz})\text{Pd}^0(\text{PPh}_3)_2$, with the overall complexation step slightly faster than the oxidative addition step ($k_1^{\text{app}}[\text{CH}_2=\text{CH-CH}_2\text{-OBz}] > k_2$). The fact that the rate constants k_1^{app} and k_2 increase with the increasing ability of the leaving groups to leave is thus consistent (Table 1, entry 11, 9, 7, 3)

Table 1. Effect of the leaving group OZ on the reaction of allyl carboxylates $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OZ}$ with Pd^0 complexes generated in situ from $\text{Pd}^0(\text{dba})_2$ ($C_0 = 1 \text{ mM}$) and 2 equiv. PPh_3 or 1 equiv. dppf or dppb , in DMF. Comparative equilibrium constants K (Eq 2) and rate constants k_1^{app} and k_2 (Scheme 1)

	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{OZ}$ -OZ ^a	Ligand	T (°C)	$10^3 \times K$ (M)	k_1^{app} ($\text{M}^{-1} \text{ s}^{-1}$)	k_2 (s^{-1})
1	-OCO ₂ Et	PPh_3	20	$\gg 10^3$	$> 100^{\text{b}}$	n.d. ^c
2	-OCO ₂ Et	PPh_3	-15	$\gg 10^3$	1.5^{d}	> 0.015
3	-OCOCF ₃	PPh_3	-10	$\gg 10^3$	40^{d}	$\gg 1$
4	-OCOCF ₃	PPh_3	20	$\gg 10^3$	$> 100^{\text{b}}$	n.d. ^c
5	-OCOCH ₂ Cl	PPh_3	20	280	$> 100^{\text{b}}$	n.d. ^c
6		PPh_3	20	150	$> 100^{\text{b}}$	n.d. ^c
7			10	n.d.	80	0.5
8		PPh_3	20	8.6	62	n.d.
9			10	n.d.	30	0.17
10		PPh_3	20	2	n.d.	n.d.
11			10	n.d.	25	0.15
12	-OCOCH ₃	PPh_3	20	0.035^{e}	n.d.	n.d.
13	-OCOCF ₃	dppf	16	340	$> 100^{\text{b}}$	n.d.
14		dppf	16	180	> 100	0.021
15		dppf	16	14	94	0.01
16	-OCOCH ₃	dppf	16	1.1^{e}	9.6^{e}	0.018^{e}
17	-OCOCF ₃	dppb	25	52	n.d. ^c	n.d. ^c
18	-OCOCH ₃	dppb	25	18^{e}	52^{e}	0.025^{e}

^a For a given ligand, the leaving groups are classified in order of decreasing ability to leave when going down the table. ^b Fast reaction: $100 \text{ M}^{-1} \text{ s}^{-1}$ is the maximum rate constant that can be determined by UV spectroscopy under our experimental conditions ($t_{1/2} = 2 \text{ s}$ for $C_0 = 1 \text{ mM}$ and $[\text{allyl-OZ}] = 5 \text{ mM}$). ^c non determined because the reaction was too fast. ^d For $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ concentrations smaller than 0.02 M (see Fig 1B).

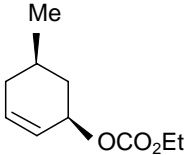
For a given bidentate ligand, either dppf (Table 1, entries 13-16) or dppb (Table 1, entries 17,18), the effect of the leaving group is the same as that observed for PPh_3 : the better the leaving group, the higher the equilibrium constant (i.e., the higher the concentration of the cationic $(\eta^3\text{-allyl})\text{Pd}(\text{P P})^+$ complex) and the higher k_1^{app} . The effect of the leaving group on the rate constant of the ionization step k_2 is consistent in the benzoates series (Table 1, entries 14,15).

Kinetics and thermodynamics of the reaction of allylic carboxylates/carbonates with Pd⁰ complexes as a function of the structure of the allylic group

For a similar leaving group and a similar ligand, either PPh₃ (Table 2, entries 1,2) or dppb (Table 2, entries 3,4), the equilibrium constant decreases, as well as k_1^{app} and k_2 , when a phenyl group is substituted on the allylic structure.

In the carbonate series (Table 2, entries 5,6), the equilibrium constant considerably decreases when the steric hindrance of the allylic carbonate increases. The steric hindrance disfavors both the complexation and ionization steps. The ionization step is faster than the complexation (Table 2, entry 7), which is consistent with the good leaving group property of the carbonate (such a situation was also encountered with the leaving group -OCOCF₃, Table 1, entry 3).

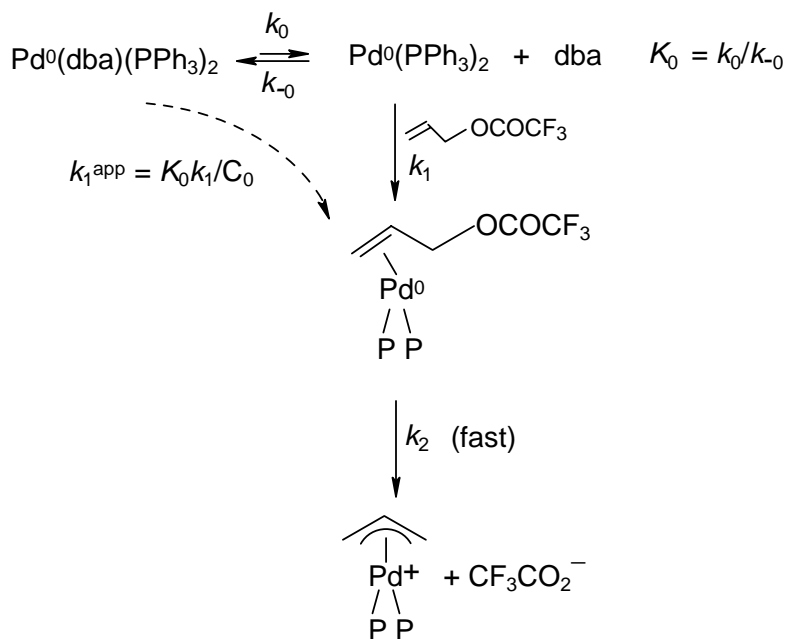
Table 2. Effect of the allylic structure on the reaction of allyl carboxylates/carbonates with Pd⁰ complexes generated in situ from Pd⁰(dba)₂ (C₀ = 1 mM) and 2 equiv. PPh₃ or 1 equiv. dppb, in DMF. Comparative equilibrium constants K (Eq 2) and rate constants k_1^{app} and k_2 (Scheme 1)

n°	allyl-OZ	Ligand	T (°C)	10 ³ × K (M)	k_1^{app} (M ⁻¹ s ⁻¹)	k_2 (s ⁻¹)
1	CH ₂ =CH-CH ₂ -OCOCH ₃	PPh ₃	20	0.035 ²	n.d.	n.d.
2	(<i>E</i>)-Ph-CH=CH-CH ₂ -OCOCH ₃	PPh ₃	20	0.02	n.d.	n.d.
3	CH ₂ =CH-CH ₂ -OCOCH ₃	dppb	25	18 ³	52	0.025
4	(<i>E</i>)-Ph-CH=CH-CH ₂ -OCOCH ₃	dppb	25	3.3	1	0.006
5	CH ₂ =CH-CH ₂ -OCO ₂ Et	PPh ₃	20	>> 10 ³	> 100	n.d. ^a
6		PPh ₃	20	0.14 ⁵	n.d. ^a	n.d. ^a
7	"	"	10	n.d.	0.73	>> 0.073

^a Non determined because the reaction was too fast.

Rate and mechanism of the reaction of the allyl trifluoroacetate to the Palladium(0) complex generated from Pd⁰(dba)₂ and 2 equiv. PPh₃ in DMF

As mentioned above, the rate of formation of the cationic complex ($\eta^3\text{-C}_3\text{H}_5$)Pd(PPh₃)₂⁺ from CH₂=CH-CH₂-OCOCF₃ (as monitored by conductivity measurements) was found to be equal to that of the disappearance of Pd⁰(dba)(PPh₃)₂ (as monitored by UV spectroscopy), whatever the allyl trifluoroacetate concentration in the range 0.05-0.16 mM. This indicates that the ionization step from the intermediate complex ($\eta^2\text{-CH}_2\text{=CH-CH}_2\text{-OCOCF}_3$)Pd⁰(PPh₃)₂ is considerably faster than the rate of formation of this complex (rate constant k_1^{app} , Scheme 2), which is then rate determining: $k_2 \gg k_1^{\text{app}}[\text{CH}_2\text{=CH-CH}_2\text{-OCOCF}_3]$. Consequently k_2 cannot be determined.



Scheme 2

Reaction of the allyl trifluoroacetate with the Pd^0 generated from $\text{Pd}^0(\text{dba})_2$ and 2 equiv. PPh_3 in DMF

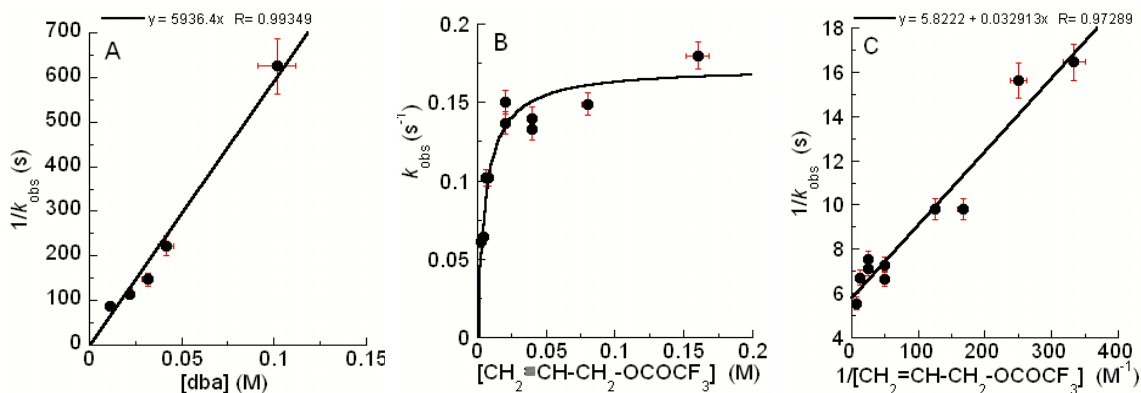


Figure 1. Kinetics of the reaction of $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ with the Pd^0 complex formed from $\text{Pd}^0(\text{dba})_2$ ($C_0=2\text{mM}$) with 2 equiv. PPh_3 in DMF, at -10°C . A) Determination of the reaction order in dba for $[\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3] = 10\text{mM}$: plot of $1/k_{\text{obs}}$ versus dba concentration. B) Determination of the reaction order in $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$: plot of k_{obs} versus $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ concentration. C) Plot of $1/k_{\text{obs}}$ versus the reciprocal of $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ concentration (Eq 4).

The reaction order in dba is -1 (Figure 1A). The reaction order in $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ was determined by plotting the observed rate constant k_{obs} (s^{-1}) of the formation of the cationic

complex *versus* $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ concentration (Figure 1B). A reaction order of +1 was found at low $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ concentrations but at higher concentrations, a saturation effect was observed with a reaction order of zero (Figure 1B). This means that at high $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ concentrations, the reaction rate is no longer determined by the complexation of $\text{Pd}^0(\text{PPh}_3)_2$ by the allyl trifluoroacetate but by the step, which delivers the reactive $\text{Pd}^0(\text{PPh}_3)_2$ (k_0 in Scheme 2). The kinetic law for the formation of the intermediate $(\eta^2-\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3)\text{Pd}^0(\text{PPh}_3)_2$ is then given in Eq 3 (allyl stands for $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$).

$$k_{\text{obs}} = \frac{k_0 k_1 [\text{allyl}]}{k_0 [\text{dba}] + k_1 [\text{allyl}]} \quad (3) \quad \frac{1}{k_{\text{obs}}} = \frac{1}{k_0} + \frac{k_0 [\text{dba}]}{k_0 k_1 [\text{allyl}]} \quad (4)$$

At low $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ and high dba concentrations: $k_0 [\text{dba}] > k_1 [\text{allyl}]$ and $1/k_{\text{obs}} = [\text{dba}]/k_1 K_0 [\text{allyl}]$. $k_1 K_0$ is then determined from the slope of the regression line of Fig 1A.^[9]
 $K_0 k_1 = 0.08 \text{ s}^{-1}$; $k_1^{\text{app}} = K_0 k_1 / C_0 = 40 \text{ M}^{-1} \text{ s}^{-1}$ in DMF at $-10 \text{ }^\circ\text{C}$

The general equation (3) is shown in reciprocal form in Eq 4. The plot of $1/k_{\text{obs}}$ *versus* the reciprocal of $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ concentration is indeed found to be linear with a positive intercept (Fig 1C), which justifies the saturating effect observed at high $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$ concentrations and supports the mechanism given in Scheme 2. k_0 is then determined from the intercept.¹⁰

$$k_0 = 0.17 \text{ s}^{-1} \text{ in DMF at } -10 \text{ }^\circ\text{C}$$

It is worthwhile to note that this is the first determination of the forward rate constant k_0 of the equilibrium between $\text{Pd}^0(\text{dba})(\text{PPh}_3)_2$ and $\text{Pd}^0(\text{PPh}_3)_2$. This determination was possible because we have, for the first time, a very reactive reagent for which, at high concentrations ($> 0.02\text{M}$), the following inequality is fulfilled: $k_1 [\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3] > k_0 [\text{dba}]$. k_0 becomes then the rate determining step of the overall reaction and can be measured experimentally.

In conclusion, the reaction of allylic carboxylates or carbonates with Pd^0 complexes (first step of the Tsuji-Trost reaction) is reversible and involves the formation of an intermediate complex $(\eta^2\text{-allyl-OZ})\text{Pd}^0(\text{P P})$ (complexation step) whatever the phosphine ligand, monodentate or bidentate, examined here. This step is followed by the formation of a cationic $(\eta^3\text{-allyl})\text{Pd}^{\text{II}}(\text{P P})^+$ complex with ZO^- as the counter anion (ionization step). The better the leaving group OZ, the higher the concentration of the cationic complex. For good leaving groups (carbonate, trifluoroacetate) the ionization step is faster than the complexation step whereas the ionization step is rate determining for poorer leaving groups (acetate, benzoate).

The reaction of cyclic allylic *carbonates* proceeds with isomerization at the allylic position.⁵ This result is not limited to the allylic carbonates since we recently observed that the reaction of

a cyclic allylic *benzoate* also proceeds with isomerization at the allylic position.¹¹ This definitively demonstrates that the role of the leaving group in Tsuji-Trost reactions is certainly more complex than usually considered and may play a significant kinetic role.

Experimental Section

General Procedures. UV spectra were recorded on a DU 7400 Beckman spectrophotometer in a thermostated 1 mm length cell. Conductivity measurements were performed with a Tacussel CD6NG Conductivity Meter. The value of the cell constant was $K = 0.9 \text{ cm}^{-1}$.

Materials. DMF was distilled from calcium hydride under vacuum and kept under argon. Commercial (Aldrich) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OAc}$, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCH}_2\text{Cl}$, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$, (*E*)- $\text{Ph}-\text{CH}=\text{CH}-\text{CH}_2-\text{OAc}$, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCO}_2\text{Et}$ were used after filtration on alumina. The ligands PPh_3 (Aldrich), dppb (Aldrich) and dppf (Strem), dba (Aldrich) were commercial. The allyl benzoates $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCO}-\text{C}_6\text{H}_5$, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCO}-\text{C}_6\text{H}_4-p\text{Me}$, and $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCO}-\text{C}_6\text{H}_4-p\text{CF}_3$ were synthesized according to described procedures¹² as well as $\text{Pd}(\text{dba})_2$.¹³

General procedure for the kinetic investigations by UV spectroscopy

All experiments were performed in DMF under Argon on solutions of $\text{Pd}^0(\text{dba})_2$ (1 mM) and PPh_3 (2 mM). After addition of the suitable amount of the allylic carboxylate at the desired temperature, the decay of the absorbance of $\text{Pd}^0(\text{dba})(\text{PPh}_3)_2$ at $\lambda = 395 \text{ nm}$ was recorded *versus* time, according to the procedure reported in previous works.²⁻⁵

General procedure for the kinetic investigations by conductivity measurements

All experiments were performed in DMF under Argon on solutions of $\text{Pd}^0(\text{dba})_2$ (1 mM) and PPh_3 (2 mM) (except for experiments reported in Figure 1 where the $\text{Pd}^0(\text{dba})_2$ concentration was 2 mM and PPh_3 concentration 4 mM). After addition of the suitable amount of the allylic carboxylate at the desired temperature, the increase of the conductivity was recorded *versus* time up to the limiting value, according to the procedure reported in previous works.²⁻⁵

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9. Since the kinetics were performed in the presence of 5 equiv. $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCOCF}_3$, the kinetic law was $\ln((4+x)/5x) = 4K_0k_1C_0t/[\text{dba}] = 4k_{\text{obs}}t^{171}$ ($C_0 = [\text{Pd}^0] = 2 \text{ mM}$; $x = [\text{Pd}^0]/[\text{Pd}^0]_0$). $1/k_{\text{obs}} = [\text{dba}]/K_0k_1C_0$. Consequently the slope of the regression line of Fig 1A is $1/K_0k_1C_0$ and $K_0k_1 = 0.08 \text{ s}^{-1}$.
10. The reaction order in allyl trifluoroacetate (Fig 1B) was determined in the absence of excess added dba in order to be able to observe the saturating effect. The dba concentration varies as the reaction proceeds from an initial concentration of 2 mM to a final concentration of 4 mM. The slope of the straight line in Fig 1C, provides the value of $[\text{dba}]/K_0k_1 = 3.3 \times 10^{-2} \text{ Ms}$. From the value of $K_0k_1 = 0.08 \text{ s}^{-1}$ determined in the conditions of Fig. 1A (excess dba), one gets an average value of $[\text{dba}] = 2.6 \text{ mM}$.
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