Journal of Organometallic Chemistry 624 (2001) 217–222

www.elsevier.nl/locate/jorganchem

Rate and mechanism of the reversible formation of a cationic (η^3-allyl)palladium(II) complex in the oxidative addition of allylic acetate to a palladium(0) complex ligated by diop: an unusual behavior

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Received 9 October 2000; accepted 7 November 2000

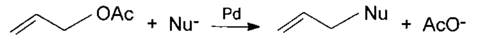
Abstract

The oxidative addition of the allyl acetate to the palladium(0) complex generated from [Pd^0(dba)$_2$] + 1 equivalent of diop gives a cationic (η^3-allyl)palladium(II) complex. This reaction is reversible and proceeds from [Pd^0(diop)] through at least three successive equilibria. The overall equilibrium constant and the rate constants of the successive steps have been determined in DMF by UV spectroscopy and conductivity measurements. The overall complexation step of the Pd^0 by the allyl acetate is faster than the formation of the cationic complex [(η^3-C$_3$H$_5$)Pd(η^2-diop)]$^+$(AcO)$^-$, which unexpectedly proceeds in two steps, i.e. not from [(η^2-CH$_2$=CH–CH$_2$–OAc)Pd^0(η^2-diop)] in contrast to other ligands (dppf or dppb) but mainly from [(η^2-CH$_2$=CH–CH$_2$–OAc)$_2$Pd^0(η^1-diop)]. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Kinetics; P,P ligand; Oxidative addition; Allyl complexes

1. Introduction

The nucleophilic substitutions on allylic acetates or derivatives (Tsuji–Trost reactions) are catalyzed by palladium complexes (Eq. (1)) [1].



(1)

We have established that the oxidative addition of the allyl acetate to the palladium(0) complex generated from [Pd^0(dba)$_2$] (dba: *trans,trans*-dibenzylideneacetone) and a monophosphine ligand [2] or diphosphine ligands (P,P) (P,P: dppb or dppf) is a reversible reaction which proceeds by three successive equilibria (Scheme 1) [3].

$$\begin{aligned}&\mathrm{Pd^0(dba)(P,P) + CH_2{=}CH{-}CH_2{-}OAc}\\&\overset{K}{\rightleftarrows} \mathrm{(\eta^3\text{-}C_3H_5)Pd(P,P)^+ + AcO^- + dba} \qquad (2)\end{aligned}$$

The equilibrium constant of the overall equilibrium (Eq. (2)), $K = K_0K_1K_2$, has been determined as well as the rate constants k_1^{app} (overall rate constant describing the complexation sequence: $k_1^{\mathrm{app}} = K_0k_1/C_0$, C_0 is the initial [Pd^0(dba)(P,P)] concentration) and k_2 (oxidative addition/ionization step) (Scheme 1) [3]. In all above cases, the reaction order in allyl acetate for the overall complexation step is 1, as expected. The intermediate neutral complex [(η^2-CH$_2$=CH–CH$_2$–OAc)Pd^0(P,P)], whose formation has been kinetically characterized, gives a cationic (η^3-allyl)palladium(II) complex: [(η^3-C$_3$H$_5$)Pd(P,P)]$^+$(AcO)$^-$, through a reaction which is slower than the overall complexation step (k_1^{app}[CH$_2$=CH–CH$_2$–OAc] > k_2). Consequently the rate of formation of the cationic complex does not depend on the allyl acetate concentration (zero reaction order) [3].

We report here mechanistic investigations on the oxidative addition of allyl acetate to the palladium(0) complex generated from [Pd^0(dba)$_2$] + one equivalent of diop (diop = (+) *O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) [4]. Unexpectedly, the

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PII: S0022-328X(00)00872-X

kinetic data obtained for this ligand do not fit the mechanism reported in Scheme 1.

2. Results and discussion

2.1. Evidences of the reversibility of the oxidative addition of allyl acetate to the palladium(0) complex formed in the mixture [Pd^0(dba)$_2$] + one equivalent of diop in DMF

As already reported, the formation of [Pd^0(dba)(diop)] from the reaction of [Pd^0(dba)$_2$] and one equivalent of diop in DMF is a slow reaction, due to the formation of an intermediate complex [Pd^0(diop)$_2$] as described in Scheme 2 [5].

Therefore, any mechanistic investigation on the reactivity of [Pd^0(dba)(diop)] in oxidative addition shall be undertaken at least 1 h after mixing [Pd^0(dba)$_2$] and diop (2 mM each in DMF) at room temperature, so that Pd^0(dba)(diop) may be formed quantitatively.

As for dppb and dppf ligand [3], the oxidative addition of the allyl acetate CH_2=CH–CH_2–OAc to the palladium(0) complex formed from [Pd^0(dba)$_2$] + one equivalent of diop gives eventually a cationic (η^3-allyl)palladium(II) complex (Eq. (3)), as evidenced by conductivity measurements. Moreover this reaction is reversible. Indeed, the conductivity of the solution increased upon successive additions of CH_2=CH–CH_2–OAc and decreased upon successive additions of dba. To be totally displaced towards the cationic complex, this equilibrium required the addition of at least 20 equivalents of CH_2=CH–CH_2–OAc. The overall equilibrium constant K (Eq. (3)) could be determined from these conductivity measurements as reported for dppf and dppb [3]: $K/C_0 = 0.85$ at 25°C.

Table 1

^{31}P-NMR shifts of the palladium(0) complex formed from [Pd^0(dba)$_2$] + 1diop and of the cationic (η^3-allyl)palladium(II) complex formed in its oxidative addition to allyl acetate in DMF. Comparison to authentic samples

Entry		δ (ppm) [a]
1	Pd^0(dba)(diop)	9.81 (d, $J_{P,P} = 14$ Hz) 8.46 (d, $J_{P,P} = 14$ Hz)
2	(η^3-C_3H_5)Pd(diop)$^+$,BF_4^- [b]	10.76 (d, $J_{P,P} = 44$ Hz) 9.86 (d, $J_{P,P} = 44$ Hz)
3	(η^3-C_3H_5)Pd(diop)$^+$,TfO$^-$ [b]	10.82 (d, $J_{P,P} = 44$ Hz) 9.88 (d, $J_{P,P} = 44$ Hz)
4	(η^3-C_3H_5)Pd(diop)$^+$,TfO$^-$ [b] + AcO$^-$ [c]	10.20 (s)
5	(η^3-C_3H_5)Pd(diop)$^+$,AcO$^-$ [d]	10.18 (s)
6	(η^3-C_3H_5)Pd(diop)$^+$,TfO$^-$ [b] + AcO$^-$ [c] + CH_2=CH–CH_2–OAc [e]	10.20 (s)
7	(η^3-C_3H_5)Pd(diop)$^+$,TfO$^-$ [b] + CH_2=CH–CH_2–OAc [e]	10.82 (d, $J_{P,P} = 44$ Hz) 9.88 (d, $J_{P,P} = 44$ Hz)
8	(η^3-C_3H_5)Pd(diop)$^+$,TfO$^-$ [b] + CH_2=CH–CH_2–OAc [e] + AcO$^-$ [c]	10.20 (s)

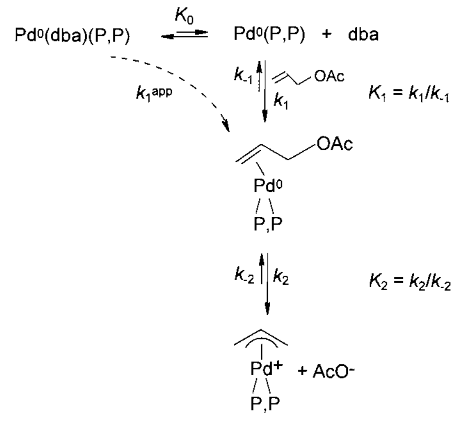
[a] Determined versus H_3PO_4 as an external standard in DMF containing 10% of acetone-d_6.

[b] Authentic sample.

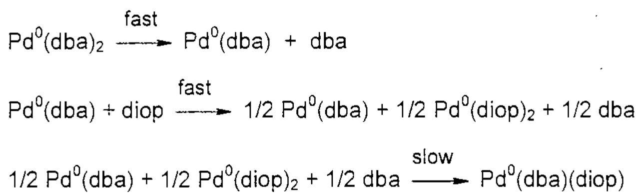
[c] One equivalent of n-Bu_4NOAc.

[d] Formed in situ from [Pd^0(dba)$_2$] + one equivalent of diop in the presence of 90 equivalents of CH_2=CH–CH_2–OAc.

[e] 90 equivalents of CH_2=CH–CH_2–OAc.



Scheme 1. Mechanism of the oxidative addition of allyl acetate to the Pd^0 complex generated from [Pd(dba)$_2$] + one equivalent of P,P (P,P = dppb, dppf).



$$\mathrm{Pd^0(dba)_2} \xrightarrow{\text{fast}} \mathrm{Pd^0(dba)} + \mathrm{dba}$$

$$\mathrm{Pd^0(dba)} + \mathrm{diop} \xrightarrow{\text{fast}} 1/2\ \mathrm{Pd^0(dba)} + 1/2\ \mathrm{Pd^0(diop)_2} + 1/2\ \mathrm{dba}$$

$$1/2\ \mathrm{Pd^0(dba)} + 1/2\ \mathrm{Pd^0(diop)_2} + 1/2\ \mathrm{dba} \xrightarrow{\text{slow}} \mathrm{Pd^0(dba)(diop)}$$

Scheme 2. Mechanism of the formation of [Pd^0(dba)(diop)].

$$\mathrm{Pd^0(dba)(diop)} + \mathrm{CH_2{=}CH{-}CH_2{-}OAc} \overset{K}{\rightleftarrows} (\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Pd(diop)^+} + \mathrm{AcO^-} + \mathrm{dba} \qquad (3)$$

Comparison to previous results shows that the overall equilibrium lies more in favor of the cationic (η^3-C_3H_5)palladium(II) complex in the order: dppb > diop > dppf > PPh_3 with $K/C_0 = 9$ [3], 0.85, 0.35 [3] and 0.035 [2], respectively ($C_0 = 2$ mM).

The cationic (η^3-allyl)palladium(II) complex [(η^3-C_3H_5)Pd(diop)]$^+$ formed in this oxidative addition, with AcO$^-$ as the counter anion, has been characterized by its ^{31}P-NMR signal [6]. A singlet was observed at 10.18 ppm (Table 1) similar to that of an authentic sample synthesized independently (vide infra, Table 1, entries 4–5).

2.2. Kinetic investigations

The kinetics of formation of the cationic complex $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+$ was monitored by conductivity measurements, under conditions where the overall reaction was irreversible, (i.e. for allyl acetate concentrations in the rang 20–100 mM), so that the reverse reactions do not interfere significantly. In contrast to what was observed for dppb and dppf [3], the kinetics was found to depend on the allyl acetate concentration. Indeed, the experimental rate constant $k_2^{\rm exp}$ (s^{-1}) of the formation of the cationic complex, determined from the conductivity data[1], was proportional to the allyl acetate concentration (Fig. 1(a)). From the slope of the regression line, the apparent rate constant for the formation of the cationic complex has been determined: $k_2^{\rm app} = 1.6$ M^{-1} s^{-1} at 25°C. A unity reaction order for the allyl acetate would easily be accounted by assuming that the ionization step is faster than the establishment of the overall complexation step through which the neutral complex $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(diop)]$ is formed (Scheme 1). However, this hypothesis was ruled down since the disappearance of $[Pd^0(dba)(diop)]$ as monitored by UV spectroscopy (at $\lambda = 425$ nm, Fig. 1(b)) was faster than the formation of the cationic complex, whatever the allyl acetate concentration (compare Fig. 1(a and b))[2]. As expected, the reaction order in allyl acetate for the disappearance of $[Pd^0(dba)(diop)]$ is 1 (Fig. 1(b)) and the corresponding apparent rate constant $k_1^{\rm app}$ equals 12 M^{-1} s^{-1} at 25°C. This means that whatever the allyl acetate concentration (in the range 20–100 mM) the formation of the cationic (η^3-allyl)palladium complex is always slower than the disappearance of the palladium(0) complex (compare $k_1^{\rm app}$ and $k_2^{\rm app}$). Consequently intermediate Pd^0 complex(es) must accumulate before the ionic species may be formed. Since both reactions have a reaction order of 1 for the allyl acetate, this indicates that the allyl acetate interferes in the oxidative addition/ionization step. This situation is then completely different from that observed for the dppb and dppf ligands for which the formation of the cationic complex was also rate determining but with a reaction order of zero in the allyl acetate [3].

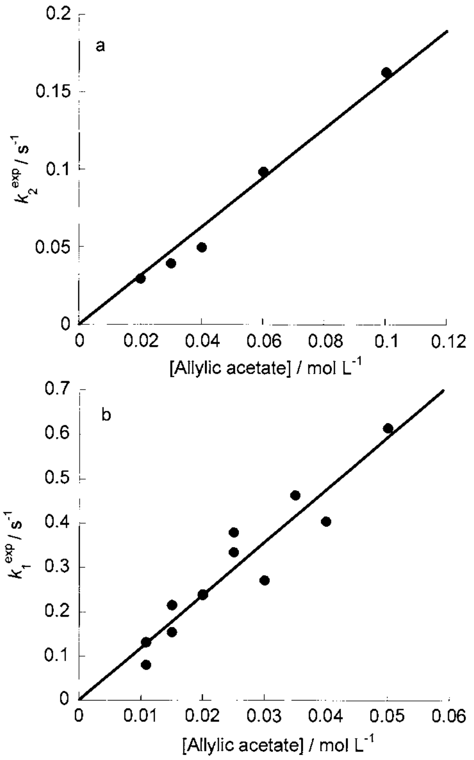
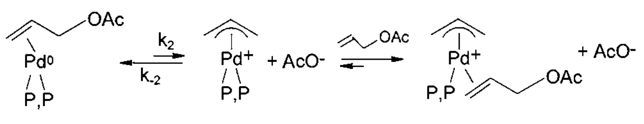


Fig. 1. Oxidative addition of $CH_2{=}CH\text{–}CH_2\text{–}OAc$ to the palladium(0) complex formed in situ from $[Pd^0(dba)_2]$ (2 mM) and diop (2 mM) in DMF at 25°C. (a) Plot of the experimental rate constant $k_2^{\rm exp}$ for the formation of $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+$, monitored by conductivity measurements, versus the $CH_2{=}CH\text{–}CH_2\text{–}OAc$ concentration. (b) Plot of the experimental rate constant $k_1^{\rm exp}$ for the disappearance of $[Pd^0(dba)(diop)]$, monitored by UV spectroscopy, versus the $CH_2{=}CH\text{–}CH_2\text{–}OAc$ concentration.



Scheme 3. Tentative hypothesis for the mechanism of the oxidative addition/ionization step from $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(diop)]$ (P,P = diop).

A first interpretation of these results would suggest that the cationic (η^3-allyl)palladium(II) complex is formed from $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(diop)]$ through an endergonic equilibrium displaced by a slow rate determining incorporation of one molecule of allyl acetate, so as to form a final complex where the Pd^+ center would be ligated by the allyl acetate, after deligation of one phosphorous of the ligand (Scheme 3).

This hypothesis was ruled out on the basis of the structure of the final complex formed in the reaction. The related complexes $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(BF_4)^-$ or $(TfO)^-$ were synthesized by reaction of diop with the dimeric complex $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ in the presence of a chloride quencher, according to the classical proce-

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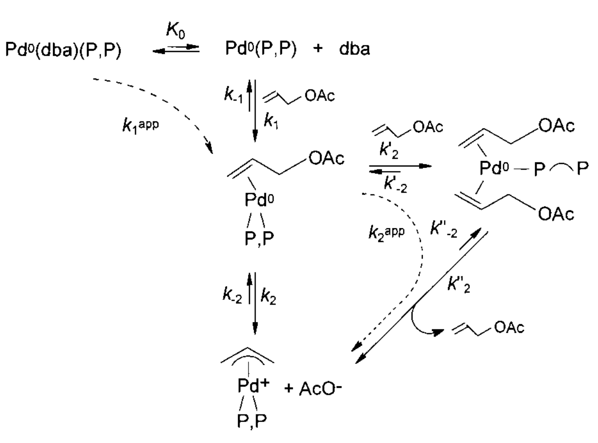
[1] $k_2^{\rm exp}$ was determined from conductivity measurements by the slope of the regression lines obtained by plotting $\ln[(\kappa_{\rm lim} - \kappa)/\kappa_{\rm lim}]$ versus time, for various concentrations of allyl acetate ($\kappa_{\rm lim}$: conductivity measured at infinite time; κ conductivity measured at t). The kinetic law for the formation of the cationic complex $[(\eta^3\text{-}C_3H_5)Pd(diop)^+]$ is: $\ln[(\kappa_{\rm lim} - \kappa)/\kappa_{\rm lim}] = -k_2^{\rm exp}t$ [3].

[2] $k_1^{\rm exp}$ was determined by UV spectroscopy (425 nm) by the slope of the regression lines obtained by plotting $2\ln[(D - D_\infty)/(D_0 - D_\infty)] + 1 - (D - D_\infty)/(D_0 - D_\infty)$ versus time, for various concentrations of allyl acetate. $(D - D_\infty)/(D_0 - D_\infty) = [Pd^0]/[Pd^0]_0$ (D = absorbance of $[Pd^0(dba)(diop)]$ at t, D_0 = initial absorbance, D_∞ = absorbance at infinite time). The kinetic law for the disappearance of $[Pd^0(dba)(diop)]$ is: $2\ln([Pd^0]/[Pd^0]_0) + 1 - [Pd^0]/[Pd^0]_0 = -k_1^{\rm exp}t$ [3].



Scheme 4. Mechanism of the oxidative addition of allyl acetate to the Pd^0 complex generated from $[Pd(dba)_2]$ + one equivalent of diop.

Table 2
Equilibrium and rate constants for the oxidative addition of allyl acetate to the Pd^0 complex generated from $[Pd^0(dba)_2]$+one equivalent of diop ($C_0 = 2$ mM) in DMF (Scheme 4 and Eq. (3)) at 25°C [a]

P,P	diop	dppf	dppb
K/C_0	0.85	0.35	9
$k_1^{app} = K_0 k_1/C_0$ (M^{-1} s^{-1})	12	8.4	26
k_2 (s^{-1})	$\ll 0.01$	1.8 (rds [b,c])	2.5 (rds [d])
k_2^{app}(M^{-1} s^{-1})	1.6 (rds [e])	$\ll 2$	$\ll 4$

[a] Comparison with dppf and dppb [3] (Scheme 1 and Eq. (2)). At 25°C except at 16°C.

[b] At 16°C.

[c] Rate determining step as soon as the allyl acetate concentration is higher than 3.8 mM.

[d] Rate determining step as soon as the allyl acetate concentration is higher than 1 mM.

[e] Rate determining step for allyl acetate concentrations higher than 20 mM.

dure used for related complexes [2,7]. Their ^{31}P-NMR spectrum exhibited two doublets of equal integration (Table 1, entries 2–3) characteristic of two diastereotopic phosphorous [8]. Addition of one equivalent of n-Bu_4NOAc to $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(TfO)^-$ in DMF modified its ^{31}P-NMR spectrum in the sense that only one singlet was observed at 10.20 ppm (Table 1, entry 4), similar to that observed for the complex formed in situ by the oxidative addition performed in the presence of an excess of allyl acetate, as reported above (Table 1, entry 5). This means that in the presence of one equivalent of AcO^-, a singlet is observed for $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(AcO)^-$ due to a scrambling effect of the counter anion or to an equilibrium between the endo and exo complex induced by the reversibility of the oxidative addition. Addition of allyl acetate (90 equivalents) to $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+$ $(AcO)^-$ formed by reaction of $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+$ $(TfO)^-$ with one equivalent of n-Bu_4NOAc did not modify the shift of the singlet signal (Table 1, entry 6), thus establishing that the structure of the cationic complex was not affected at all by the presence of a large excess of allyl acetate. In another series of experiments, allyl acetate (90 equivalents) was added to $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(TfO)^-$ in DMF. Again, the ^{31}P-NMR spectrum was not modified and the two doublets characteristic of $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(TfO)^-$ were still observed (Table 1, entries 7 and 3). This establishes again that no reaction occurs between the allyl acetate and $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(TfO)^-$. Addition then of one equivalent of n-Bu_4NOAc to this mixture resulted in the formation of the singlet characteristic of $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(AcO)^-$ as observed above (Table 1, entry 8). Both sets of NMR experiments show that the allyl acetate does not react with $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+$ in the absence or presence of AcO^- to form the final complex postulated in Scheme 3. The complex $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(AcO)^-$ is definitively the final complex formed in the oxidative addition of the allyl acetate to $[Pd^0(dba)(diop)]$, even in the presence of large excess of allyl acetate. Thus the mechanism of the oxidative addition/ionization step cannot follow the tentative mechanism of Scheme 3.

We are thus led to consider that the unity reaction order of the allyl acetate, observed for the formation of the cationic complex, reflects a pre-complexation of the intermediate $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(diop)]$ complex (Scheme 4). The intermediate complex $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(\eta^2\text{-}diop)]$ formed in a fast reaction, incorporates a second molecule of allyl acetate (after cleavage of a Pd^0–P bond) to afford an intermediate 16-electron Pd^0 complex $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)_2Pd^0(\eta^1\text{-}diop)]$ (k'_2 as the rate constant) which ultimately gives the cationic $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(AcO)^-$ complex through the oxidative addition/ionization step (k''_2 as the rate constant) (Scheme 4).

Assuming a steady state behavior for the intermediate complex: $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)_2Pd^0(\eta^1\text{-}diop)]$, one obtains: $d([\underline{A}])/dt = -k_2^{app}[CH_2{=}CH\text{–}CH_2\text{–}OAc][\underline{A}]$ where $\underline{A} = (\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(\eta^2\text{-}diop)]$ and $k_2^{app} = k'_2 k''_2/(k'_{-2} + k''_2)$ for the apparent rate constant of formation of the cationic complex. This mechanism is consistent with all the above kinetic data. However, we cannot discriminate between a kinetic irreversibility of the incorporation of the second molecule of allyl acetate followed by a fast oxidative addition/ionization step ($k''_2 > k'_{-2}$, then $k_2^{app} = k'_2$) or the situation where $k''_2 < k'_{-2}$ (then $k_2^{app} = k'_2 k''_2/k'_{-2}$) i.e. an equilibrated incorporation of the second molecule of allyl acetate displaced by a slow ionization step.

One has $k_2^{app} = 1.6$ M^{-1} s^{-1} (determined above, Fig. 1(a)) whereas $k_1^{app} = k_1 K_0/C_0 = 12$ M^{-1} s^{-1} (determined above, Fig. 1(b)) at 25°C (Table 2), with $k_1^{app} > k_2^{app}$ whatever the allyl acetate concentration.

However, the direct formation of the cationic complex $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(AcO)^-$ from the intermediate complex $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(\eta^2\text{-}diop)]$ (with the rate constant k_2 in Scheme 4) cannot be completely ruled out. Indeed, the addition of ten equivalents of AcO^- and two equivalents of dba to a solution of $[(\eta^3\text{-}C_3H_5)Pd(diop)]^+(TfO)^-$ resulted in the formation of $[Pd^0(dba)(diop)]$ characterized by its two ^{31}P-NMR signals (Table 1, entry 1) [5]. According to the principle of microscopic reversibility, this means that the overall reverse reaction can also proceed in the absence of allyl acetate. This establishes the feasibility of the direct formation of the cationic complex from $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(\eta^2\text{-}diop)]$ (rate constant k_2 in Scheme 4). However, such a direct oxidative addition/ionization step from $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(\eta^2\text{-}diop)]$ must be a slow reaction relative to that observed here since the linear plot of the observed rate constant (k_2^{exp}) versus the allyl acetate concentration passes through origin within the precision of its determination (Fig. 1(a)). The kinetic contribution of the direct ionization step (rate constant k_2) should indeed be observed as a positive intercept [5]. Thus, there is definitely a competition at the level of the complex $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(\eta^2\text{-}diop)]$ ($\underline{A}$) between a first order ionization step whose rate is $k_2[\underline{A}]$ and a second reaction order whose rate is $k'_2[\underline{A}][CH_2{=}CH\text{–}CH_2\text{–}OAc]$, the contribution of the latter reaction being predominant at high allyl acetate concentrations as investigated here or under true catalytic conditions.

3. Conclusion

In DMF, the oxidative addition of allyl acetate to the palladium(0) complex generated from $[Pd(dba)_2]$ + one equivalent of diop gives a cationic $[(\eta^3\text{-}C_3H_5)Pd(P,P)]^+(OAc)^-$ complex through a reversible process involving at least four successive equilibria (Scheme 4). A neutral intermediate complex $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(\eta^2\text{-}diop)]$ is formed in a fast initial reaction, followed by the slow formation of the cationic complex: $[(\eta^3\text{-}C_3H_5)Pd(\eta^2\text{-}diop)]^+(AcO)^-$. However, this latter reaction requires one additional molecule of allyl acetate. Indeed, in contrast to the dppf or dppb ligands, the oxidative addition/ionization step does not take place intramolecularly within $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(\eta^2\text{-}diop)]$ but mainly through the transient formation of $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)_2Pd^0(\eta^1\text{-}diop)]$, followed by the formation of the cationic $[(\eta^3\text{-}C_3H_5)Pd(\eta^2\text{-}diop)]^+$ with AcO^- as the counter anion.

Whatever the bidentate P,P ligand (dppf, dppb, diop), the final complex formed in the reaction of $Pd^0(P,P)$ to allyl acetate is always the cationic complex $[(\eta^3\text{-}C_3H_5)Pd(P,P)]^+$ with AcO^- as the counter anion. However, the mechanism of the rate determining step of the overall oxidative addition is affected by the ligand (for dppb or dppf, see k_2 in Table 2 and k_2^{app} for diop). It is up to now not clear why the neutral complex $[(\eta^2\text{-}CH_2{=}CH\text{–}CH_2\text{–}OAc)Pd^0(\eta^2\text{-}diop)]$ does incorporate a second molecule of allyl acetate after cleavage of one Pd^0–P bond before undergoing its ionization step. Indeed, on the basis of its electronic properties (basicity in the order: dppf > diop ≈ dppb) and steric factors (bite angles P–Pd–P which decrease in the order: dppf > diop > dppb [9]), diop does not appear as really different in this series.

4. Experimental

4.1. General

^{31}P-NMR spectra were recorded on a Bruker spectrometer (101 MHz) using H_3PO_4 as an external reference. UV spectra were recorded on a DU 7400 Beckman spectrophotometer. Conductivity was measured on a Tacussel CDM210 conductivity meter (cell constant = 1 cm^{-1}).

4.2. Chemicals

DMF was distilled from calcium hydride under vacuum and kept under argon. Commercial allyl acetate $CH_2{=}CH\text{–}CH_2\text{–}OAc$ (Acros) was used after filtration on alumina. Commercial $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ and diop (Acros) were used without any purification. $[Pd^0(dba)_2]$ was prepared according to described procedures [10]. The synthesis of $[(\eta^3\text{-}C_3H_5)Pd(diop)](BF_4)$ and $[(\eta^3\text{-}C_3H_5)Pd(diop)](TfO)$ was adapted from related procedures [2,7].

4.3. $[(\eta^3\text{-}C_3H_5)Pd(diop)](BF_4)$

A solution of 0.125 g (0.25 mmol) of diop in 3 ml of acetone was added to a solution of 50 mg (0.13 mmol) of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ in 2 ml of acetone. 4 ml of water were then added, followed by 0.161 g (1.5 mmol) of $NaBF_4$ in 2 ml of water, leading to the formation of a precipitate. Crystallization from dichloromethane/petroleum ether afforded pale yellow crystals of pure $[(\eta^3\text{-}C_3H_5)Pd(diop)][BF_4]$. The complex was characterized by ^{31}P-NMR spectroscopy (Table 1).

4.4. $[(\eta^3\text{-}C_3H_5)Pd(diop)](TfO)$

The same procedure was used for the synthesis of $[(\eta^3\text{-}C_3H_5)Pd(diop)](BF_4)$ using 258 mg (1.5 mmol) of NaOTf. The complex was characterized by ^{31}P-NMR spectroscopy (Table 1).

4.5. *UV experiments*

They were performed in a thermostated 1 mm path length cell on mixtures of [Pd^0(dba)$_2$] (2 mmol dm^{-3}) and one equivalent of diop in DMF and the suitable amount of CH_2=CH–CH_2–OAc.

Acknowledgements

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).

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