Rate and Mechanism of the Reversible Formation of Cationic (η^3-Allyl)palladium Complexes in the Oxidative Addition of Allylic Acetate to Palladium(0) Complexes Ligated by Diphosphanes

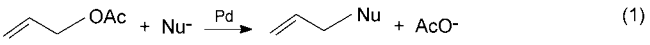
Christian Amatore,* Sophie Gamez, and Anny Jutand*[a]

Abstract: The oxidative addition of the allylic acetate, $CH_2{=}CH{-}CH_2{-}OAc$, to the palladium(0) complex $[Pd^0(P,P)]$, generated from the reaction of $[Pd(dba)_2]$ with one equivalent of P,P (P,P = dppb = 1,4-bis(diphenylphosphanyl)butane, and P,P = dppf = 1,1′-bis(diphenylphosphanyl)ferrocene), gives a cationic (η^3-allyl)palladium(II) complex, $[(\eta^3\text{-}C_3H_5)Pd(P,P)^+]$, with AcO^- as the counter anion. This reaction is reversible and proceeds through two successive equilibria. The overall equilibrium constants have been determined in DMF. Compared with PPh_3, the overall equilibrium lies more in favor of the cationic (η^3-allyl)palladium(II) complex when bidentate P,P ligands are considered in the order: dppb > dppf > PPh_3. The reaction proceeds via a neutral intermediate complex $[(\eta^2\text{-}CH_2{=}CH{-}CH_2{-}OAc)Pd^0(P,P)]$, which has been kinetically detected. 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 allylic acetate C=C bond is faster than the oxidative addition/ionization step which gives the cationic (η^3-allyl)palladium(II) complex.

Keywords: allyl complexes • kinetics • oxidative addition • palladium • P,P ligands

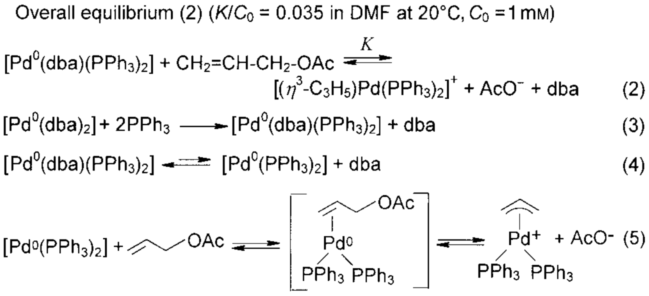
Introduction

Palladium complexes are efficient catalysts in nucleophilic substitutions on allylic acetates or derivatives (Tsuji–Trost reactions) [Eq. (1)].[1] We have established that the oxidative

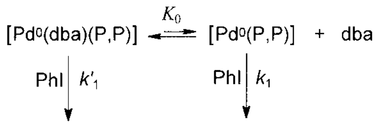


addition of the allylic acetate $CH_2{=}CH{-}CH_2{-}OAc$ to the palladium(0) complex generated from $[Pd^0(dba)_2]$ and two equivalents of PPh_3 (dba = *trans,trans*-dibenzylideneacetone) is a reversible reaction, which gives a cationic (η^3-allyl)palladium(II) with AcO^- as the counter anion [Eq. (2) in Scheme 1].[2] This reaction proceeds by successive equilibria via the putative intermediate $[(\eta^2\text{-}CH_2{=}CH{-}CH_2{-}OAc)Pd^0(PPh_3)_2]$ [Eqs. (4) and (5) in Scheme 1].[2] The oxidative addition to allylic carbonates is also reversible and proceeds with isomerization at the allylic position.[3]

$[Pd^0(dba)_2]$, when associated with bidentate diphosphane ligands (P,P), generates efficient catalytic precursors for Tsuji–Trost reactions and chiral diphosphanes induce enantioselective reactions.[1, 4] The reactive species generated from the reaction of $[Pd^0(dba)_2]$ with one equivalent of P,P ligand have been identified through a mechanistic investigation of their oxidative addition to PhI.[5] $[Pd^0(P,P)]$ and $[Pd^0(dba)(P,P)]$ are involved in an equilibrium, and both complexes react in parallel with PhI. However $[Pd^0(P,P)]$ is the more reactive complex ($k_1 >> k'_1$) (Scheme 2).[5]



Scheme 1. Oxidative addition of allylic acetate to the Pd^0 complex generated from $[Pd^0(dba)_2]$ and two equivalents of PPh_3.



Scheme 2. Reactive complexes in oxidative addition.

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Here we report investigations of the mechanism of the oxidative addition of allylic acetates to the palladium(0) complexes generated from the reaction between $[Pd(dba)_2]$ and one equivalent of P,P (P,P = dppb = 1,4-bis(diphenylphosphanyl)butane and P,P = dppf = 1,1′-bis(diphenylphosphanyl)ferrocene). We establish that cationic (η^3-allyl)palladium(II) complexes are formed in a multistep reversible oxidative addition.

Results and Discussion

Reversibility of the oxidative addition of allylic acetate to the palladium(0) complex formed from the reaction of $[Pd^0(dba)_2]$ with one equivalent of dppb

Kinetic investigations: As for the reaction of $[Pd^0(dba)_2]$ and two equivalents of PPh_3, the oxidative addition of allylic acetate $CH_2{=}CH{-}CH_2{-}OAc$ to the palladium(0) complexes generated from the reaction of $[Pd^0(dba)_2]$ with one equivalent of dppb was monitored by conductivity measurements to characterize the formation of ionic species. ^{31}P and ^1H NMR spectroscopy were used to characterize the allylpalladium(II) complex formed in the oxidative addition, and UV spectroscopy was used to monitor the reactivity of the active palladium(0) complex with the allylic acetate.

As previously reported, the formation of $[Pd^0(dba)(dppb)]$ from the reaction of $[Pd^0(dba)_2]$ and one equivalent of dppb in DMF or THF is a slow reaction because of the formation of the intermediate complex $[Pd^0(dppb)_2]$ (Scheme 3).[5]

$$[Pd^0(dba)_2] \xrightarrow{\text{fast}} [Pd^0(dba)] + dba \qquad (6)$$

$$[Pd^0(dba)] + dppb \xrightarrow{\text{fast}} 1/2\,[Pd^0(dba)] + 1/2\,[Pd^0(dppb)_2] + 1/2\,dba \qquad (7)$$

$$1/2\,[Pd^0(dba)] + 1/2\,[Pd^0(dppb)_2] + 1/2\,dba \xrightarrow{\text{slow}} [Pd^0(dba)(dppb)] \qquad (8)$$

Scheme 3. Mechanism of the formation of $[Pd^0(dba)(dppb)]$.

Therefore any mechanistic investigation of the reactivity of $[Pd^0(dba)(dppb)]$ in oxidative addition should be undertaken at least 45 min after mixing $[Pd^0(dba)_2]$ and one equivalent of dppb (2 mM each in DMF) at room temperature.

The conductivity κ of a solution of $[Pd^0(dba)(dppb)]$ (2 mM), formed from $[Pd^0(dba)_2]$ (2 mM) and dppb (2 mM) in DMF, increased after addition of five equivalents of allylic acetate and reached a limiting value (Figure 1; $n = 5$). This limiting value increased slightly after addition of five more equivalents of allylic acetate, but remained unchanged after a third addition of five equivalents of allylic acetate (Figure 1). The limiting conductivity of the solution decreased upon successive additions of n' equivalents of dba (Figure 1). These experiments demonstrate the formation of ionic species that are involved in an equilibrium with the starting reagents, because their concentration increases upon increasing the allylic acetate concentration [Eq. (9)]. Moreover, dba, whose effect is to decrease the concentration of the ionic species, accompanied by the formation of increasing amounts of $[Pd^0(dba)(dppb)]$ (vide infra), is involved in the reverse reaction of this equilibrium [Eq. (9)].

$$[Pd^0(dba)(dppb)] + CH_2{=}CH{-}CH_2{-}OAc \overset{K}{\rightleftharpoons} [(\eta^3\text{-}C_3H_5)Pd(dppb)]^+ + AcO^- + dba \qquad (9)$$

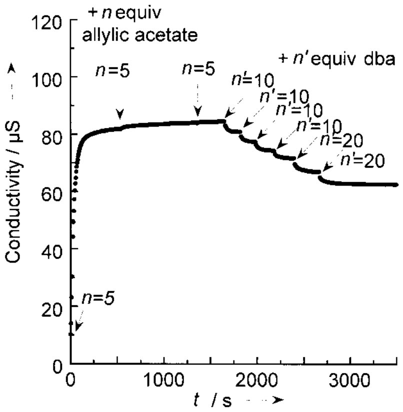


Figure 1. Conductivity measurements in DMF at 25 °C. Initially: $[Pd(dba)_2]$ (2 mM) and dppb (2 mM), then successive additions of n equivalents of $CH_2{=}CH{-}CH_2{-}OAc$ as indicated by the arrows ($0 < t < 1500$ s) followed by successive additions of n' equivalents of dba as indicated by the arrows ($t > 1500$ s).

The ^{31}P NMR spectrum of a solution of $[Pd^0(dba)_2]$ and one equivalent of dppb in DMF exhibited the two signals of equal magnitude for $[Pd^0(dba)(dppb)]$ at $\delta = 21.7$ and 18.0 due to the monoligation of dba (Table 1).[5] After addition of 44 equivalents of $CH_2{=}CH{-}CH_2{-}OAc$, only a single signal was observed at $\delta = 21.5$, which was assigned to the cationic (η^3-allyl)palladium complex $[(\eta^3\text{-}C_3H_5)Pd(dppb)]^+(AcO^-)$ by comparison with a pure sample of $[(\eta^3\text{-}C_3H_5)Pd(dppb)]BF_4$ ($\delta = 21.7$). This latter complex was synthesized by treatment of $[\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)\}_2]$ with two equivalents of dppb in the presence of a chloride ion scavenger.[6] Starting from a solution of $[(\eta^3\text{-}C_3H_5)Pd(dppb)]BF_4$ in DMF, which exhibited a single signal at $\delta = 21.7$, addition of two equivalents of nBu_4NOAc and 10 equivalents of dba resulted in two signals at $\delta = 21.7$ and 18, characteristic of $[Pd^0(dba)(dppb)]$. This establishes the occurrence of the reverse reaction of the equilibrium [Eq. (9)]. The magnitude of the signal at $\delta = 21.7$ was higher than that of the signal at $\delta = 18$, although they have the same magnitude for $[Pd^0(dba)(dppb)]$ alone. This means that the equilibrium [Eq. (9)] was not completely shifted towards $[Pd^0(dba)(dppb)]$. The signal of the cationic complex at $\delta = 21.7$ was then still observed, overlapping one of the two

Table 1. ^{31}P NMR shifts of the Pd^0 complexes formed from the reaction of $[Pd(dba)_2]$ and one equivalent of P,P and of the cationic (η^3-allyl)palladium(II) complexes formed in the oxidative addition to allylic acetate in DMF. The results are compared to those obtained from the reaction of $[Pd(dba)_2]$ and two equivalents of PPh_3.[2]

δ[a]	dppb	dppf	PPh_3
$[Pd^0(dba)(P,P)]$[b]	21.7 and 18.0	20.7 and 18.3	27.4 and 25.5
$[(\eta^3\text{-}C_3H_5)Pd(P,P)]^+(AcO^-)$[b]	21.5	24.2	24.1
$[(\eta^3\text{-}C_3H_5)Pd(P,P)]BF_4$[c]	21.7	24.3	24.1

[a] Determined versus H_3PO_4 as an external standard in DMF containing 10% of $[D_6]$acetone. [b] Formed in situ. [c] Authentic sample.

signals of [Pd^0(dba)(dppb)] at $\delta = 21.7$, and was responsible for the higher magnitude of the signal at $\delta = 21.7$ when compared with that at $\delta = 18$.

The reaction of [(η^3-C$_3$H$_5$)Pd(dppb)]BF$_4$ with acetate ions was also monitored by UV spectroscopy in DMF. A solution of [(η^3-C$_3$H$_5$)Pd(dppb)]BF$_4$ (2 mM) did not exhibit any absorbance band at around 400 nm. After addition of five equivalents of dba and five equivalents of nBu$_4$NOAc, the absorption band characteristic of [Pd^0(dba)(dppb)] at $\lambda = 385$ nm appeared. These two last experiments give clear evidence that a palladium(0) complex is formed by attack of the acetate ion on the cationic (η^3-allyl)palladium complex (reverse reaction of the equilibrium in Equation (9)).

Although oxidative additions of allylic acetates to Pd^0 complexes ligated by diphosphane ligands are usually considered to be irreversible,[1a] we have established that the oxidative addition of the allylic acetate to the Pd^0 complex formed from the reaction of [Pd(dba)$_2$] and one equivalent of dppb is a reversible reaction. The equilibrium constant K of the overall equilibrium [Eq. (10)] (P,P = dppb) could be determined from conductivity measurements, using the data in Figure 1.

$$[\mathrm{Pd^0(dba)(P,P)}] + \mathrm{CH_2{=}CH{-}CH_2{-}OAc} \overset{K}{\rightleftharpoons} [(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Pd(P,P)}]^+ + \mathrm{AcO^-} + \mathrm{dba} \qquad (10)$$

Denoting n as the total number of equivalents of CH$_2$=CH–CH$_2$–OAc, n' that of added dba, x_{eq} the equilibrium concentration of [(η^3-C$_3$H$_5$)Pd(P,P)$^+$] and AcO$^-$ relative to the initial concentration C_0 of [Pd^0(dba)(P,P)], one obtains [Eq. (11)].

$$K = \frac{[(\eta^3\text{-C}_3\text{H}_5)\text{Pd(P,P)}^+][\text{AcO}^-][\text{dba}]}{[\text{Pd(dba)(P,P)}][\text{CH}_2{=}\text{CH–CH}_2\text{–OAc}]} = \frac{x_{\mathrm{eq}}^2(1 + x_{\mathrm{eq}} + n')C_0}{(1 - x_{\mathrm{eq}})(n - x_{\mathrm{eq}})} \qquad (11)$$

Note that at equilibrium, [dba] = $(1+x_{\mathrm{eq}}+n')C_0$ since one equivalent of dba is released during the generation of [Pd(dba)(P,P)] from [Pd(dba)$_2$] [Eqs. (6)–(8); see Scheme 1]. In addition, $x_{\mathrm{eq}} = \kappa_{\mathrm{eq}}/\kappa_{\mathrm{irrev}}$, where κ_{eq} is the conductivity measured when the equilibrium [Eq. (10)] is fully established in the presence of CH$_2$=CH–CH$_2$–OAc ($n = 15$; $10 < n' < 80$) and κ_{irrev} the conductivity when the equilibrium [Eq. (10)] is totally displaced towards its right-hand side, ($n = 15$, $n' = 0$). The value of K was then calculated from the slope of the regression line obtained by plotting $x_{\mathrm{eq}}{}^2/(1 - x_{\mathrm{eq}})$ versus $(n - x_{\mathrm{eq}})/(1+x_{\mathrm{eq}}+n')C_0$ (Figure 2; $K/C_0 = 9 \pm 1$ at 25 °C for dppb; Table 2).

Therefore, the oxidative addition of allylic acetate to a palladium(0) complex is reversible when the palladium(0) center is ligated by two monophosphane ligands (e.g., PPh$_3$)[2] as well as by a bidentate phosphane ligand such as dppb. However the equilibrium lies more in favor of the cationic (η^3-allyl)palladium complex when the palladium center is ligated by dppb (Table 2).

When the time scale of the initial part of the curve in Figure 1 was extended ($0 < t < 100$ s), an S-shaped curve is observed for the kinetics of the formation of the ionic species (Figure 3, curve b). This is clear evidence of the involvement of at least one neutral intermediate complex on the way to the cationic (η^3-allyl)palladium(II) complex. This prompted us to investigate the kinetics of the reaction of the palladium(0)

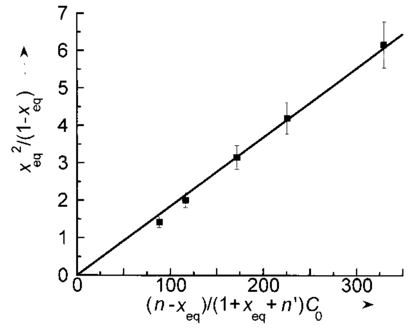


Figure 2. Determination of the overall equilibrium constant K for the oxidative addition of CH$_2$=CH–CH$_2$–OAc to the palladium(0) complex formed in situ from [Pd(dba)$_2$] ($C_0 = 2$ mM) and dppb (2 mM), in the presence of n equivalents of CH$_2$=CH–CH$_2$–OAc and n' equivalents of added dba in DMF at 25 °C [Eq. (9)], using the conductivity data of Figure 1. Plot of $x_{\mathrm{eq}}{}^2/(1 - x_{\mathrm{eq}})$ versus $(n - x_{\mathrm{eq}})/(1+x_{\mathrm{eq}}+n')C_0$ [Eq. (11)]. $x_{\mathrm{eq}} = \kappa_{\mathrm{eq}}/\kappa_{\mathrm{irrev}}$, κ_{eq}: conductivity measured when the equilibrium [Eq. (9)] is fully established in the presence of CH$_2$=CH–CH$_2$–OAc ($n = 15$; $10 < n' < 80$) and κ_{irrev}: conductivity when the equilibrium [Eq. (9)] is totally displaced towards its right-hand side ($n = 15$, $n' = 0$).

Table 2. Equilibrium and rate constants for the oxidative addition of allylic acetate to the Pd^0 complex generated from the reaction of [Pd(dba)$_2$] and one equivalent of P,P in DMF (Scheme 5, Equation (10), $C_0 = 2$ mM). The results are compared to those obtained from the reaction of [Pd(dba)$_2$] and two equivalents of PPh$_3$.[2]

P,P	dppb		dppf			PPh$_3$
T [°C]	3	25	10	16	25	20
K/C_0		9	1	0.53	0.35	0.017
$10^2 \times K_0k_1$ [s^{-1}]	1.6	5.8		1.0	1.7	
$k_1{}^{\mathrm{app}}$ [M^{-1}s^{-1}]	8	26		4.8	8.4	
$10^2 \times k_2$ [s^{-1}]		2.5[a]		1.8[b]		
$k_1{}^{\mathrm{app}}/k_2$ [M^{-1}]	1050		270			

[a] Rate-determining step as soon as the allylic acetate concentration is higher than 1 mM. [b] Rate-determining step as soon as the allylic acetate concentration is higher than 3.8 mM.

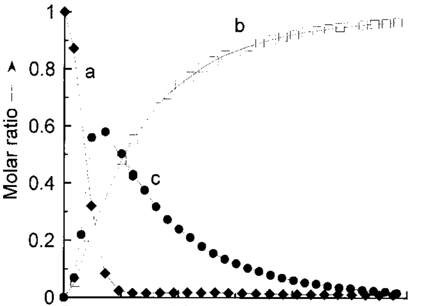
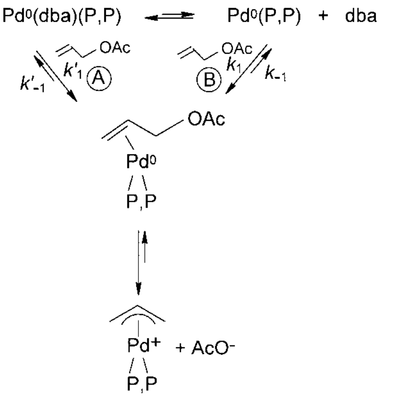


Figure 3. Oxidative addition of CH$_2$=CH–CH$_2$–OAc (10 mM) to the palladium(0) complex formed in situ from [Pd(dba)$_2$] (2 mM) and dppb (2 mM) in DMF at 25 °C. a) (◆) Molar ratio of [Pd^0(dba)(dppb)] versus time, determined by UV spectroscopy at 425 mm, in a 1 mm path cell. b) (□) Molar ratio of the cationic complex [(η^3-C$_3$H$_5$)Pd(dppb)$^+$](OAc$^-$) versus time, determined by conductivity measurements. c) (●) Molar ratio of the neutral intermediate complex [(η^2-CH$_2$=CH–CH$_2$–OAc)Pd^0(dppb)] versus time, determined from curves a and b of Figure 3 (see text).

center with the allylic acetate by UV spectroscopy. The complex [Pd^0(dba)(dppb)], quantitatively formed in a mixture of [Pd^0(dba)$_2$] and one equivalent of dppb (2 mM each in DMF), was characterized by UV spectroscopy by its absorption band at $\lambda_{max} = 385$ nm. Addition of five equivalents of $CH_2{=}CH{-}CH_2{-}OAc$ to this solution at 25 °C resulted in a decay of the absorbance of [Pd(dba)(dppb)] of up to 2 % of its initial value (curve a in Figure 3) with a half-reaction time of $t_{1/2} = 8$ s. The rate of disappearance of the palladium(0) in its reaction with five equivalents of allylic acetate is thus faster than the rate of formation of the ionic species monitored by conductivity measurements (curve b in Figure 3, $t_{1/2} = 25$ s). This again demonstrates the involvement of an intermediate (neutral because it does not give rise to any increase of the solution conductivity) in the overall reaction (9). The evolution of the concentration of this neutral intermediate versus time could be deduced from the complement of the sum of curves a and b to the total amount of palladium (see curve c in Figure 3). Even though this intermediate complex could not be characterized due to its too short half-life time, it is presumably an adduct in which the palladium(0) is ligated to the C=C bond of the allylic acetate as in [(η^2-$CH_2{=}CH{-}CH_2{-}OAc$)Pd^0(P,P)], in agreement with usual literature consensus.[1, 7] Note that such a neutral intermediate was not kinetically detected when the ligand was PPh_3.[2]

Since [Pd^0(dba)(P,P)] is the major complex involved in an equilibrium with [Pd^0(P,P)] and since both complexes were found to be reactive in the oxidative addition to PhI (Scheme 2),[4] a question arises about the formation of the intermediate Pd^0 adduct by a S_N1- or S_N2-type mechanism. Indeed this may occur either from [Pd^0(dba)(P,P)] (route A), from [Pd^0(P,P)] (route B), or from both complexes (Scheme 4).



Scheme 4. The two possible routes for the reaction of allylic acetate to the Pd^0 complexes generated from [Pd(dba)$_2$] and one equivalent of P,P ligand.

Discrimination between routes A and B in Scheme 4 was achieved after a detailed kinetic investigation of this reaction. The rate of disappearance of [Pd^0(dba)(dppb)] over time was monitored by UV spectroscopy ($\lambda = 425$ nm) as a function of the dba and the allylic acetate concentrations ([$CH_2{=}CH{-}CH_2{-}OAc$] > 10 mM), under conditions where reactions A or B were totally shifted towards the formation of the allylic acetate/Pd^0 adduct, as attested by the complete disappearance of the UV absorption band of [Pd^0(dba)(dppb)] at the end of the reaction. The backward reactions (rate constants k_{-1} and k'_{-1} in Scheme 4) could then be neglected. In the absence of added dba, plotting the experimental rate constant k_{exp} (s^{-1}) versus the allylic acetate concentration afforded a straight line passing through the origin (Figure 4a). Consequently the reaction order in the allylic acetate was found to be 1. This establishes that only one Pd^0 complex is involved in the complexation of the allylic acetate C=C bond. On the other hand, k_{exp}/[$CH_2{=}CH{-}CH_2{-}OAc$] varied linearly versus the reciprocal of dba concentration for various concentrations of allylic acetate (Figure 4b). The reaction order in dba is thus −1, which indicates that [Pd^0(dppb)] is the only reactive species (route B), under conditions where the whole reaction is irreversible. Based on the principle of microscopic reversibility, route B must also be followed during the reverse reaction. Consequently, the overall oxidative addition of the allylic acetate to the palladium(0) complex formed from the reaction between [Pd(dba)$_2$] and one equivalent of dppb is a reversible reaction, which proceeds through a sequence of three reversible steps (Scheme 5). The first two steps correspond to an S_N1-type substitution of the dba ligand by the allylic acetate, which presumably coordinates through its C=C double bond. It is followed by the true oxidative addition step (also called the ionization step), which is also reversible and gives ionic species (Scheme 5).

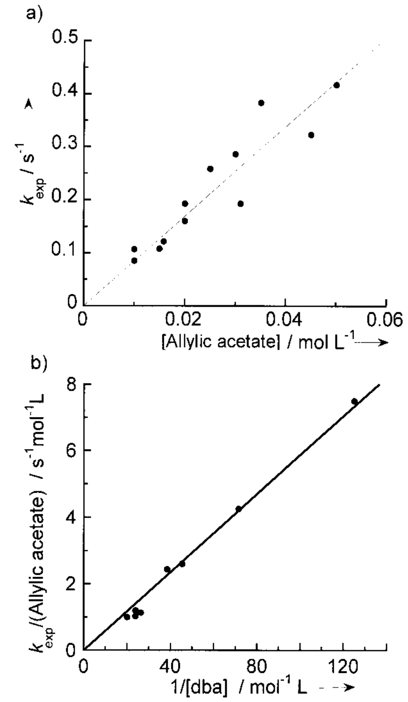
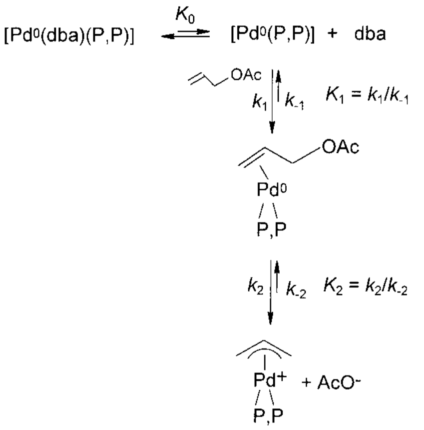


Figure 4. Oxidative addition of $CH_2{=}CH{-}CH_2{-}OAc$ to the palladium(0) complex formed in situ from [Pd(dba)$_2$] (2 mM) and dppb (2 mM) in DMF, under conditions where the overall reaction is irreversible ([$CH_2{=}CH{-}CH_2{-}OAc$] > 10 mM). a) Plot of the experimental rate constant k_{exp} for the disappearance of [Pd^0(dba)(dppb)], monitored by UV spectroscopy, versus $CH_2{=}CH{-}CH_2{-}OAc$ concentration, at 3 °C. b) Plot of the experimental rate constant k_{exp} for the disappearance of [Pd^0(dba)(dppb)] monitored by UV spectroscopy versus the reciprocal of dba concentration at 25 °C.



Scheme 5. Mechanism of the oxidative addition of allylic acetate to the Pd^0 complex generated from [Pd(dba)$_2$] and one equivalent of P,P ligand (P,P = dppb, dppf). Overall equilibrium: $K = K_0K_1K_2$ in Equation (10).

Based on Scheme 5, the disappearance of the Pd^0 complex in the presence of allylic acetate obeys the kinetic law in Equations (12a) and (12b) when dba is in excess. From the slope of the regression line obtained in Figure 4b, one therefore readily determines $K_0k_1 = 5.8 \times 10^{-2}\,\mathrm{s}^{-1}$ at 25 °C (Table 2).

$$\ln([\mathrm{Pd}^0]/[\mathrm{Pd}^0]_0) = -k_{exp}t = -K_0k_1[\mathrm{CH_2{=}CH{-}CH_2{-}OAc}]t/[\mathrm{dba}] \quad (12a)$$

$$\text{with } k_{exp}/[\mathrm{CH_2{=}CH{-}CH_2{-}OAc}] = K_0k_1/[\mathrm{dba}] \quad (12b)$$

In the absence of added dba, the concentration of dba varies as the reaction proceeds because of the progressive displacement of the equilibrium between [Pd^0(dba)(dppb)] and [Pd^0(dppb)]. The disappearance of the Pd^0 complex obeys then the kinetic law in Equations (13a) and (13b).[8] From the slope of the regression line obtained in Figure 4a, one has $K_0k_1 = 1.6 \times 10^{-2}\,\mathrm{s}^{-1}$ at 3 °C (Table 2).

$$2\ln([\mathrm{Pd}^0]/[\mathrm{Pd}^0]_0)+1-[\mathrm{Pd}^0]/[\mathrm{Pd}^0]_0 = -K_0k_1[\mathrm{CH_2{=}CH{-}CH_2{-}OAc}]t/C_0 = -k'_{\mathrm{exp}}t \quad (13a)$$

$$\text{with } k'_{\mathrm{exp}} = K_0k_1[\mathrm{CH_2{=}CH{-}CH_2{-}OAc}]/C_0 \quad (13b)$$

Since K_0 and k_1 cannot be determined but only K_0k_1, one can only determine the apparent rate constant k_1^{app} for the overall formation of [(η^2-CH$_2$=CH–CH$_2$–OAc)Pd^0(dppb)] from [Pd^0(dba)(dppb)] via [Pd^0(dppb)] [Eq. (14)]. k_1^{app} is given by the kinetic law of Equation (15). By comparison to Equation (13b) one gets: $k_1^{\mathrm{app}} = K_0k_1/C_0 = 8\,\mathrm{M}^{-1}\mathrm{s}^{-1}$ at 3 °C (Table 2).

$$\mathrm{Pd}^0(\mathrm{dba})(\mathrm{P,P}) + \mathrm{CH_2{=}CH{-}CH_2{-}OAc} \xrightarrow{k_1^{\mathrm{app}}} (\eta^2\text{-}\mathrm{CH_2{=}CH{-}CH_2{-}OAc})\mathrm{Pd}^0(\mathrm{P,P}) + \mathrm{dba} \quad (14)$$

$$2\ln([\mathrm{Pd}^0]/[\mathrm{Pd}^0]_0)+1-[\mathrm{Pd}^0]/[\mathrm{Pd}^0]_0 = -k_1^{\mathrm{app}}[\mathrm{CH_2{=}CH{-}CH_2{-}OAc}]t \quad (15)$$

The rate constant of the oxidative addition/ionization step (k_2 in Scheme 5) has been determined by conductivity measurements under conditions where the overall reaction was irreversible ($n = 40$ equivalents of allylic acetate) so that the reverse reactions (rate constants k_{-1} and k_{-2}) could be neglected. Under such conditions, the *S*-shaped curve, previously obtained in Figure 3b for the kinetics of formation of the cationic [(η^3-C$_3$H$_5$)Pd(dppb)$^+$] complex, was not observed (Figure 5a) because the formation of [(η^2-CH$_2$=CH–CH$_2$–OAc)Pd^0(dppb)] [Eq. (14)] was considerably faster than the oxidative addition/ionization step of [(η^2-CH$_2$=CH–CH$_2$–OAc)Pd^0(dppb)]. This latter reaction was then the rate-determining step of the overall sequence and its rate constant k_2 could then be readily determined from the conductivity data of Figure 5a. Plotting $\ln((\kappa_{\mathrm{lim}} - \kappa)/\kappa_{\mathrm{lim}})$ versus time gave a straight line (κ_{lim}: conductivity measured at the end of the reaction; κ: conductivity measured at time t) passing through the origin (Figure 5b): $\ln((\kappa_{\mathrm{lim}} - \kappa)/\kappa_{\mathrm{lim}}) = -k_2t$. The value of k_2 could then be readily determined from the slope of the regression line: $k_2 = 2.5\ (\pm 0.1) \times 10^{-2}\,\mathrm{s}^{-1}$ at 25 °C (Table 2). It was checked that within experimental accuracy, the rate of formation of the cationic [(η^3-C$_3$H$_5$)Pd(dppb)$^+$] complex, monitored by conductivity measurements, did not depend on the concentration of the allylic acetate in the range 0.02–0.1 M ($10 < n < 50$). This confirms a posteriori that the two steps of complexation and oxidative addition/ionization proceed successively on different time scales, the oxidative addition/ionization step being slower (rds) than the overall complexation step. As soon as the allylic acetate concentration is higher than 1 mM, then $k_1^{\mathrm{app}}[\mathrm{CH_2{=}CH{-}CH_2{-}OAc}] > k_2$ when P,P = dppb.

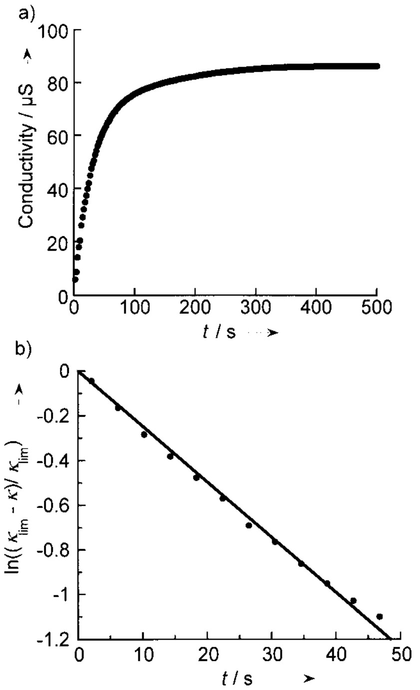


Figure 5. Kinetics of the formation of [(η^3-C$_3$H$_5$)Pd(dppb)$^+$](AcO$^-$)] by the oxidative addition of CH$_2$=CH–CH$_2$–OAc to the palladium(0) complex formed in situ from [Pd(dba)$_2$] (2 mM) and dppb (2 mM) in DMF at 25 °C under conditions where the overall reaction is irreversible ([CH$_2$=CH–CH$_2$–OAc] = 80 mM). a) Conductivity of the solution as a function of time. b) Plot of $\ln((\kappa_{\mathrm{lim}} - \kappa)/\kappa_{\mathrm{lim}})$ versus time (κ_{lim}: conductivity measured at the end of the reaction; κ: conductivity measured at time t). $\ln((\kappa_{\mathrm{lim}} - \kappa)/\kappa_{\mathrm{lim}}) = -k_2t$ (Scheme 5, Table 2).

Reversibility of the oxidative addition of allylic acetate to the palladium(0) complex formed from the reaction of [Pd^0(dba)$_2$] and one equivalent of dppf

Kinetic investigations: A similar strategy was used to investigate the mechanism of the oxidative addition of the allylic acetate $CH_2{=}CH{-}CH_2{-}OAc$ to the palladium(0) complex generated from [Pd^0(dba)$_2$] and one equivalent of dppf. The mechanism is very similar to that established above for dppb (Scheme 5), involving only different values for the equilibrium and rate constants. The overall equilibrium constant K was determined from conductivity measurements as explained above for dppb. K_0k_1 and k_1^{app} were determined from UV spectroscopy and k_2 from conductivity measurements under conditions where the reverse reactions of the complexation and ionization steps were not operating (see above).

The complex [Pd^0(dba)(dppf)] was quantitatively formed from the reaction of [Pd^0(dba)$_2$] and one equivalent of dppf (2mM each in DMF) through a fast reaction [Eq. (16)], which was complete upon mixing.[5]

$$[\mathrm{Pd^0(dba)_2}] + \mathrm{dppf} \rightarrow [\mathrm{Pd^0(dba)(dppf)}] + \mathrm{dba} \qquad (16)$$

The conductivity of a solution containing [Pd^0(dba)$_2$] and one equivalent of dppf (2mM each in DMF) increased after successive additions of the allylic acetate, attesting again to the formation of ionic species. Fifty equivalents of allylic acetate were required to observe a complete shift of the equilibrium [Eq. (17)] towards the right-hand side.

$$[\mathrm{Pd^0(dba)(dppf)}] + \mathrm{CH_2{=}CH{-}CH_2{-}OAc} \overset{K}{\rightleftharpoons} [(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Pd(dppf)}]^+ + \mathrm{AcO^-} + \mathrm{dba} \qquad (17)$$

In agreement with the formulation in Equation (17), successive additions of dba induced a decay of the conductivity plateau. The equilibrium constant K of the overall equilibrium [Eq. (17)] could thus be obtained from such conductivity data, as detailed above for dppb (vide supra, Equation (11)). $K/C_0 = 0.35 \pm 0.01$ at 25 °C for dppf. The value of K/C_0 is temperature dependent (Table 2) and increases when the temperature decreases, characterizing an exothermic reaction.

The involvement of the cationic (η^3-allyl)palladium(II) complex formed in this reaction has been established by ^{31}P NMR spectroscopy (Table 1) by comparison to an authentic sample with BF_4^- as the counter anion: [(η^3-C$_3$H$_5$)Pd(dppf)]BF$_4$ whose ^{31}P NMR single signal in DMF is located at $\delta = 24.3$. After addition of 10 equivalents of nBu$_4$NOAc and two equivalents of dba to a solution of [(η^3-C$_3$H$_5$)Pd(dppf)]BF$_4$ in DMF, two signals at $\delta = 20.8$ and $\delta = 18.5$ characteristic of [Pd^0(dba)(dppf)][5] developed at the expense of the cationic complex signal. This confirms the existence of the overall reverse reaction of the equilibrium in Equation (17).

The rate of formation of the cationic complex [(η^3-C$_3$H$_5$)Pd(dppf)]$^+$(AcO$^-$) in the presence of 50 equivalents of allylic acetate, that is when the overall equilibrium was totally shifted towards the formation of the cationic complex, was monitored by conductivity measurements. The kinetic curve exhibited an S-shaped form (Figure 6a), demonstrating the formation of an intermediate Pd^0 adduct [(η^2-$CH_2{=}CH{-}CH_2{-}OAc$)Pd^0(dppf)][7] as in Scheme 5. The rate constant k_2 could then be calculated from these conductivity data, again by plotting $\ln((\kappa_{\mathrm{lim}} - \kappa)/\kappa_{\mathrm{lim}})$ versus time (Figure 6b) and only considering the part of the curve obtained at longest times ($t > 150$ s, beyond the inflection point) for which the formation of the cationic complex was no longer limited by the faster formation of [(η^2-$CH_2{=}CH{-}CH_2{-}OAc$)Pd^0(dppf)] (vide supra). Under such conditions, $\ln((\kappa_{\mathrm{lim}} - \kappa)/\kappa_{\mathrm{lim}}) = -k_2t$ and $k_2 = 1.8 \times 10^{-2}\,\mathrm{s^{-1}}$ was then determined at 16 °C (Table 2).

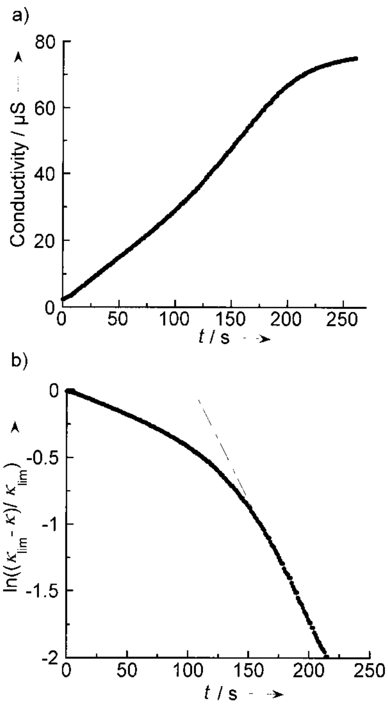


Figure 6. Kinetics of the formation of [(η^3-C$_3$H$_5$)Pd(dppf)$^+$](AcO$^-$)] by the oxidative addition of $CH_2{=}CH{-}CH_2{-}OAc$ to the palladium(0) complex formed in situ from [Pd(dba)$_2$] (2mM) and dppf (2mM) in DMF at 16 °C under conditions where the overall reaction is irreversible ([$CH_2{=}CH{-}CH_2{-}OAc$] = 100mM). a) Conductivity of the solution as a function of time. b) Plot of $\ln((\kappa_{\mathrm{lim}} - \kappa)/\kappa_{\mathrm{lim}})$ versus time (κ_{lim}: conductivity measured at the end of the reaction; κ: conductivity measured at time t). At $t > 150$ s, $\ln((\kappa_{\mathrm{lim}} - \kappa)/\kappa_{\mathrm{lim}}) = -k_2t$ (Scheme 5, Table 2).

The rate of disappearance of [Pd^0(dba)(dppf)] in the overall oxidative addition to allylic acetate was monitored by UV spectroscopy ($\lambda = 400$ nm) at 16 °C. The reaction order in the allylic acetate is one (Figure 7). $K_0k_1 = 10^{-2}\,\mathrm{s^{-1}}$ and $k_1^{app} = 4.8(\pm 0.2) \times 10^{-2}\,\mathrm{M^{-1}s^{-1}}$ were calculated from the slope of the regression line of Figure 7 (Table 2). Again the ionization step is the rate-determining one as soon as the allylic acetate concentration exceeds a few mM. Indeed, k_1^{app}[$CH_2{=}CH{-}CH_2{-}OAc$] $> k_2$ provided the allylic acetate concentration is higher than 3.6mM.

Even though the rate constants k_1^{app} and k_2 were determined at different temperatures for dppb and dppf (25 °C and 16 °C, respectively, Table 2), for identical allylic acetate concentrations the ratio k_1^{app}/k_2 is higher for dppb than for dppf (Table 2). This means that the rates of the overall complexation step and oxidative addition/ionization step are closer for dppf than for dppb, in agreement with the more pronounced sigmoïdal character of Figure 6a (dppf) as

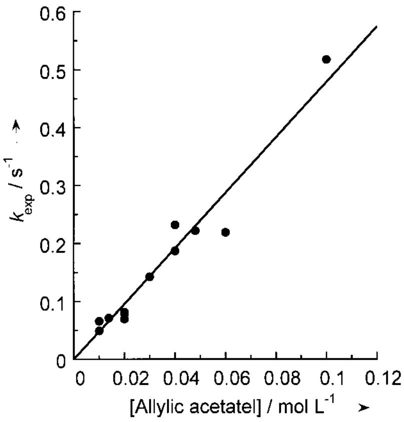


Figure 7. Oxidative addition of CH_2=CH–CH_2–OAc to the palladium(0) complex formed in situ from [Pd(dba)$_2$] (2 mM) and dppf (2 mM) in DMF at 16 °C. Plot of the experimental rate constant k_{exp} for the disappearance of [Pd^0(dba)(dppf)], monitored by UV spectroscopy, versus CH_2=CH–CH_2–OAc concentration.

compared with Figure 5a (dppb). The overall equilibrium constant K is approximately 25 times smaller for dppf than for dppb at 25 °C (Table 2).

Conclusion

In DMF, the oxidative addition of allylic acetate to the palladium(0) complex generated from the reaction of [Pd^0(dba)$_2$] and one equivalent of P,P (P,P = dppb, dppf) proceeds from [Pd^0(P,P)] and eventually gives cationic (η^3-allyl)palladium(II) complexes [(η^3-C_3H_5)Pd(P,P)$^+$] with AcO$^-$ as the counter anion, by a reversible process involving at least two successive equilibria (Scheme 5). Compared with the case with PPh$_3$,[2] the overall equilibrium lies more in favor of the cationic (η^3-allyl)palladium(II) complex for the bidentate P,P ligands considered in this work, with the order: dppb > dppf > PPh$_3$. Therefore, acetate ions react with (η^3-allyl)palladium(II) complexes with either bidentate or monodentate phosphane ligands to restore the allylic acetate and Pd^0 complexes. Under the usual catalytic conditions where the concentration of the allylic acetate is considerably higher than that of the palladium catalyst, the overall oxidative addition may be then considered as irreversible for the P,P ligands investigated here. However, as the catalytic reaction proceeds, acetate ions are continuously released in solution. Their concentration increases and they may then compete with poor or stabilized nucleophiles (whose concentration decreases as the reaction proceeds) in the nucleophilic attack of cationic (η^3-allyl)palladium(II) complexes. If the reversible oxidative addition proceeds with partial isomerization at the allylic position, as established for allylic carbonates,[3] acetate ions may then interfere in enantioselective processes. The stereochemistry of the reaction of acetate ions with cationic (η^3-allyl)palladium(II) complexes is under investigation.

For all ligands considered herein, our kinetic data establish the fast initial formation of intermediate [(η^2-CH_2=CH–CH_2–OAc)Pd^0(P,P)] complexes where the Pd^0 is ligated to the C=C bond of the allylic acetate. This is followed by the slow formation of the cationic (η^3-allyl)palladium(II) complexes. For dppb, as soon as the allylic acetate concentration is higher than 10 mM, the overall Pd^0 complexation step [Eq. (14)] occurs at least 10 times faster than the oxidative addition/ionization step (k_2 in Scheme 5), which is then the rate-determining step of the overall process. In the case of dppf, the oxidative addition/ionization step is also rate-determining but more than 40 mM of allylic acetate are required to observe clean kinetic control by the oxidative addition/ionization step, indicating that the time scales of the two successive reactions are comparatively closer for dppf than for dppb.

For identical allylic acetate concentrations, the rate of formation of [(η^2-CH_2=CH–CH_2–OAc)Pd^0(P,P)] complexes varies in the order: dppb > dppf (compare $k_1^{app} = K_0k_1/C_0$ in Table 2). The rate of this reaction depends on both the intrinsic affinity of [Pd^0(P,P)] for the allylic acetate C=C bond (rate constant k_1) and on its concentration given by K_0. Only K_0k_1 could be determined (Table 2). Neglecting steric effects in a first approach, the affinity of [Pd^0(P,P)] for the C=C bond (k_1) should increase when the basicity of the phosphane decreases.[9] On the other hand, K_0 usually increases when the basicity of the ligand decreases.[8b] Therefore K_0k_1 should increase when the basicity of the ligand decreases. The basicity order is: dppf > dppb. The more basic ligand is dppf and k_1^{app} is indeed found to be the smallest for dppf.

The rate constants of the oxidative addition/ionization step (compare k_2 in Scheme 5 and Table 2) are very similar for dppb and dppf. For any oxidative addition performed from a low-valent metal ligated by a bidentate ligand, the more basic the ligand and the smaller the bite angle, the faster the oxidative addition. In the present case, the basicity order is dppf > dppb, whereas the bite angle order is dppb < dppf.[10] As a consequence of those two opposing effects, the rate of the oxidative addition step does not depend significantly on the ligand dppb or dppf.

Experimental Section

General: 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 [{Pd(η^3-C_3H_5)(μ-Cl)}$_2$] (Acros) was used without any purification. [Pd(dba)$_2$][11] and [(η^3-C_3H_5)Pd(dppb)]BF$_4$[6] were prepared according to described procedures. The synthesis of [(η^3-C_3H_5)Pd(dppf)]BF$_4$ was adapted from a related procedure.[2, 12] ^{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 measurements were performed with a Tacussel CD6NG conductimeter. The cell constant was determined to be 0.9. UV experiments were performed in a thermostated 1 mm path length cell on mixtures of [Pd(dba)$_2$] (2 mM) and one equivalent of dppb or dppf in DMF and the suitable amount of CH_2=CH–CH_2–OAc. A UV experiment was performed from a solution of [(η^3-C_3H_5)Pd(dppb)]BF$_4$ (2 mM) containing five equivalents of dba and five equivalents of nBu$_4$NOAc.

Synthesis of [(η^3-C_3H_5)Pd(dppf)]BF$_4$: A solution of dppf (0.28 g, 0.5 mmol) in acetone (28 mL) was added to a solution of [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (0.1 g, 0.25 mmol) in acetone (5 mL). NaBF$_4$ (0.48 g, 4.5 mmol) in water (6 mL) was added, leading to the formation of a pale yellow precipitate. The solid complex was dissolved in dichloromethane and precipitated in petroleum ether. Two molecules of the complex [(η^3-C_3H_5)Pd(dppf)]BF$_4$ crystallize with one molecule of dichloromethane. ^{1}H NMR (250 MHz, [D$_1$]CHCl$_3$, TMS): δ = 3.48 (m, 2H; H *syn*), 4.03 (br. d, J = 7.4 Hz, 2H; H *anti*), 4.19 (d, 2H; Cp-H), 4.40 (d, 2H; Cp-H), 4.44 (d, 2H; Cp-H), 4.48 (d, 2H; Cp-H), 5.30 (s, 1H; 1/2CH_2Cl_2, extra signal), 5.89 (tt, $J = 15$ and 7.4 Hz, 1H; internal H), 7.41–7.62 (m, 20H; aromatic H); ^{31}P NMR: (see Table 1); elemental analysis (%) calcd for $C_{37}H_{35}BF_4FeP_2Pd \cdot 1/2\,CH_2Cl_2$ (833.16): calcd: C 54.1, H 4.3; found: C 53.80, H 4.28.

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[9] Nonactivated alkenes (such as allylic acetate) are nucleophilic reagents and their affinity for Pd^0 complexes will be higher when the Pd^0 center is less electron rich, that is, when ligated by phosphane ligands of lower basicity. However, the back-donation Pd^0 → alkene will be weaker in the case of phosphane ligands of low basicity. It seems that the effect of the back-donation is less important for the stabilization of the alkene/Pd^0 complexes. Indeed, as an example, the ligand diop is less basic than dppf and the complex [(η^2-$CH_2{=}CH_2$)Pd^0(diop)] has been isolated (see:M. Hodgson, D. Parker, R. J. Taylor, G. Ferguson, *J. Chem. Soc. Chem. Commun.* **1987**, 1309–1311), whereas [(η^2-$CH_2{=}CH_2$)Pd^0(dppf)] is only stable below room temperature.[7a]

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