CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600153

Rate and Mechanism of the Reaction of Alkenes with Aryl Palladium Complexes Ligated by a Bidentate P,P Ligand in Heck Reactions

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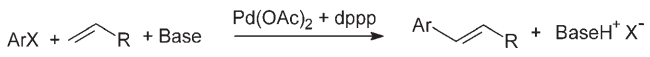
Abstract: The regioselectivity of the Heck reaction is supposed to be highly affected by the electronic properties of the alkene and the ionic or neutral character of the aryl palladium(II) complexes involved in the reaction with alkenes. In Heck reactions performed in dmf, $[Pd(dppp)\{dppp(O)\}Ph]^+$ (dppp = 1,2-bis(diphenylphosphino)propane) is generated in the oxidative addition of PhI with $[Pd^0(dppp)(OAc)]^-$ formed in situ from $Pd(OAc)_2$ associated to two equivalents of dppp. $[Pd(dppp)\{dppp(O)\}Ph]^+$ is not very reactive with alkenes (styrene or methyl acrylate); however, it reacts with iodide ions (released in the catalytic reactions) to give [Pd(dppp)IPh] and with acetate ions (used as base) to give [Pd(dppp)(OAc)Ph]. [Pd(dppp)(OAc)Ph] reacts with styrene and methyl acrylate exclusively by an ionic mechanism, that is, via the cationic complex $[Pd(dppp)(dmf)Ph]^+$ formed by dissociation of the acetate ion. The reaction of [Pd(dppp)IPh] is more complex and substrate dependent. It reacts with styrene exclusively by the ionic mechanism via $[Pd(dppp)(dmf)Ph]^+$. [Pd(dppp)IPh] (neutral mechanism) and $[Pd(dppp)(dmf)Ph]^+$ (ionic mechanism) react in parallel with methyl acrylate. $[Pd(dppp)(dmf)Ph]^+$ is more reactive than [Pd(dppp)IPh] but is always generated at lower concentration.

Keywords: Heck reaction · kinetics · P ligands · palladium · regioselectivity

Introduction

The catalytic precursor $Pd(OAc)_2$ associated with bidentate P,P ligands is used to catalyze Heck reactions.[1] Among them, the ligand 1,2-bis(diphenylphosphino)propane (dppp) proves to be very efficient (Scheme 1).[2] Two mechanisms are proposed in the literature for the reaction of alkenes with aryl palladium(II) complexes formed in the oxidative addition of $[Pd^0(P,P)]$ with ArX (X = I, Br, Cl): 1) a neutral mechanism for [Pd(P,P)X(Ar)] complexes generated from ArX[1b,e,2a–d] or ArOTf (Tf = trifluoromethanesulfonyl) in the presence of halide ions[3] (Scheme 2), or 2) an ionic mechanism for cationic complexes $[Pd(P,P)S(Ar)]^+$ (S = solvent) generated in the oxidative addition of aryl triflates[1b,e,2,4] or aryl halides in the presence of a halide scavenger (Ag^+,[5a] Tl^+,[2b,5b] or K^+ in aqueous dmf[2j]; Scheme 3).[6]



Scheme 1.

The ionic mechanism is supported by reactions of isolated complexes $[Pd(P,P)S(Ar)]^+$ with alkenes.[7,8] The intermediate complexes formed in the carbopalladation step have been characterized at low temperatures (Schemes 3 and 4a,a′).[7,8] An investigation of the ionic mechanism involving electron-deficient alkenes by Brown and Hii revealed that the β-H elimination occurs from $[Pd(dppf)(thf)(CHR\text{-}CH_2Ar)]^+$ leading to $[Pd(dppf)(S)H]^+$, which cannot restore a Pd^0 complex in the absence of a base. Consequently, $[Pd(dppf)(S)H]^+$ reacts with the initial alkene (Scheme 4a).[7a] Åkermark has also observed that $[Pd(dppp)(dmf)H]^+$ reacts with styrene in the absence of a base (Scheme 4a′).[8] In the presence of a base, a Pd^0 complex is generated directly due to the easier deprotonation of the agostic hydrogen atom, thus bypassing the β-H elimination, as proposed by Brown et al. (Scheme 4b).[7c]

The regioselectivity of Heck reactions may be affected by the mechanism: ionic versus neutral.[1b,e,2,9] Branched alkenes are usually produced from electron-rich alkenes

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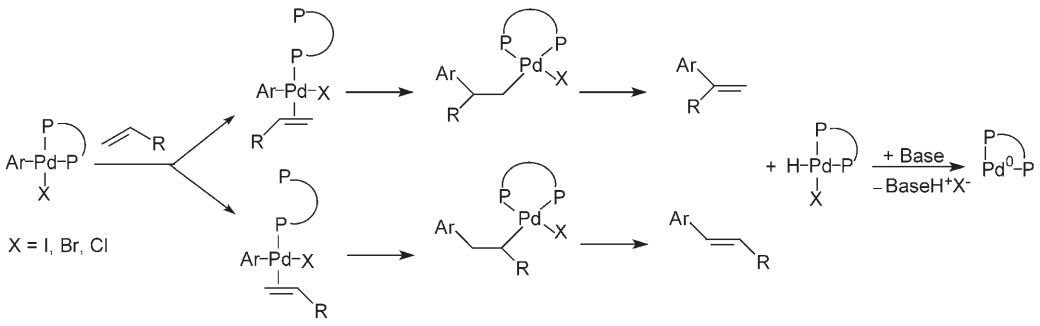
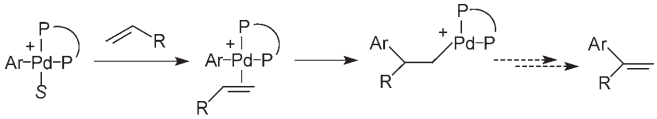
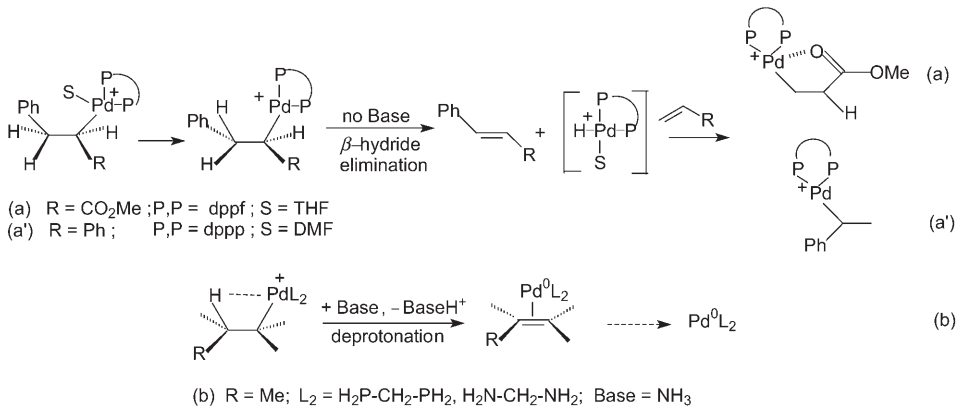


Scheme 2. Neutral mechanism.



Scheme 3. Ionic mechanism (R = electron-donating group).

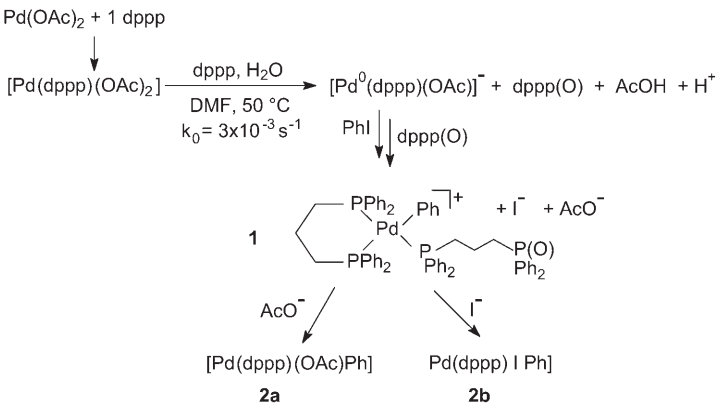


Scheme 4. Ionic mechanism. a) Experimental work. a′) Experimental work; the branched complex was also formed. b) Density functional theory (DFT) calculations. dppf = 1,1′-bis(diphenylphosphino)ferrocene.

under the conditions of the ionic mechanism (Scheme 3).[1e,2f–k] As far as electron-poor alkenes are concerned, the origin of the regioselectivity is more tricky.[1,2,9] The reaction of [Pd(dppp)XPh] (X = I, OAc, BF_4) with styrene has been investigated by Åkermark et al., who focused on the effect of X on the regioselectivity of the reaction.[8] In dmf, the ratio PhCH=CHPh/CH_2=CPh_2 was found to decrease when going from X = I, OAc to BF_4. However, no kinetic data were provided on the relative reactivity of such neutral and cationic complexes.

Most mechanisms described above were postulated or established from isolated complexes [Pd(P,P)X(Ar)] and do not take into account the real conditions of catalytic reactions. In particular, the role of acetate ions, delivered by Pd-$(OAc)_2$ (during the formation of the active Pd^0 species from this precursor) or by the base, is bypassed. Contrastingly, we have previously established that an anionic Pd^0 complex $[Pd^0(dppp)(OAc)]^-$ was formed instead of the postulated $[Pd^0(dppp)]$ whenever the catalytic precursor $Pd(OAc)_2$ is associated with two equivalents of dppp.[10a] The complex [Pd(dppp)$(OAc)_2$] is reduced to a Pd^0 complex through an intramolecular reaction which generates the hemioxide (O)PPh_2–$(CH_2)_3$–PPh_2, denoted dppp(O) (Scheme 5).[10a]

The existence and stability of the anionic complexes $[Pd^0$-(dppp)$(OAc)]^-$ have recently been supported by theoretical calculations (DFT).[11] The main complex formed in its oxidative addition with iodobenzene is $[Pd(dppp)\{dppp(O)\}Ph]^+$ (**1**).[10a] [Pd(dppp)(OAc)Ph] (**2a**) is formed when the oxidative addition is performed in the presence of excess acetate ions (Scheme 5).[1,2] Conversely, [Pd(dppp)IPh] (**2b**) is generated in the presence of excess iodide ions.[10a] Consequently, three complexes might potentially react with the alkene in a Heck reaction, depending on the exact reaction conditions: 1) the primary complex $[Pd(dppp)\{dppp(O)\}(Ar)]^+$ formed in the early step of the oxidative addition, 2) [Pd(dppp)(OAc)(Ar)] generated in the presence of acetate ions when used as a base, and/or 3) [Pd-



Scheme 5.

(dppp)I(Ar)] generated in the course of the catalytic reaction due to the release of iodides from ArI.

The purpose of this work is to compare the reactivity of the three aryl palladium(II) complexes mentioned above with alkenes and to delineate the relative contribution of the neutral and ionic mechanisms in the context of real catalytic reactions (precursor, base, ions released in the reaction, ionic strength, etc.).

Results and Discussion

Characterization of the equilibrium between [Pd(dppp)IPh] and [Pd(dppp)(OAc)Ph] in dmf: As mentioned in the Introduction, [Pd(dppp)IPh] (**2b**) and [Pd(dppp)(OAc)Ph] (**2a**) may be generated in the oxidative addition of PhI with $[Pd^0(dppp)(OAc)]^-$.[10a] As evidenced by ^{31}P NMR spectroscopy, addition of acetate ions (introduced as nBu$_4$NOAc) to isolated [Pd(dppp)IPh] resulted in the formation of [Pd(dppp)(OAc)Ph] in dmf, whereas [Pd(dppp)IPh] was generated by addition of iodide ions (introduced as nBu$_4$NI) to isolated [Pd(dppp)(OAc)Ph]. Therefore, **2a** and **2b** are in equilibrium with the corresponding ions (Scheme 6).

$$\underset{\mathbf{2b}}{[Pd(dppp)I\,Ph]} + AcO^- \overset{K}{\rightleftharpoons} \underset{\mathbf{2a}}{[Pd(dppp)(OAc)Ph]} + I^-$$

Scheme 6.

The equilibrium constant $K=([\mathbf{2a}][I^-]/[\mathbf{2b}][OAc^-])_{equil}=0.09$ (dmf, 25 °C) was determined from ^{31}P NMR spectroscopic data. [Pd(dppp)IPh] is thus thermodynamically more stable than [Pd(dppp)(OAc)Ph] at comparable I^- and AcO^- concentrations.[12] The I^-/OAc^- exchange in [Pd(dppp)IPh] probably proceeds via the cationic complex [Pd(dppp)(dmf)Ph]$^+$ (**3**$^+$, Scheme 7), as proposed for the related complex [Pd(PPh$_3$)$_2$IPh].[13]

$$\underset{\mathbf{2b}}{[Pd(dppp)I\,Ph]} \overset{K_1}{\rightleftharpoons} \underset{\mathbf{3^+}}{[Pd(dppp)(dmf)Ph]^+} + I^-$$

Scheme 7.

However, the complex **3**$^+$ must be a transient intermediate present at very low concentration, as the ^{31}P NMR spectrum of [Pd(dppp)IPh] or [Pd(dppp)(OAc)Ph] exhibited only one set of two doublets at 25 °C (Supporting Information). Nevertheless, despite such a low concentration, [Pd(dppp)(dmf)Ph]$^+$ may be formed and displaced continuously by its reaction with a competing reagent. If so, the same continuous displacement may be performed electrochemically whenever the cationic palladium species is reducible. A significant reduction wave may be observed, whose current intensity will not represent the thermodynamic concentration of [Pd(dppp)(dmf)Ph]$^+$, but the rate at which this species may be formed (chemical–electrochemical mechanism).[14] This has been addressed in full detail in the case of [Pd(PPh$_3$)$_2$IPh].[13] Consequently, the cyclic voltammogram of [Pd(dppp)IPh] (2 mM) was obtained in dmf containing nBu$_4$NBF$_4$ (0.3 M). It exhibited a major reduction peak R_2 at $E^p_{R2}=-2.10$ V versus a saturated calomel electrode (SCE) at the scan rate of 0.2 V s^{-1} (Figure 1a). Importantly, a minor

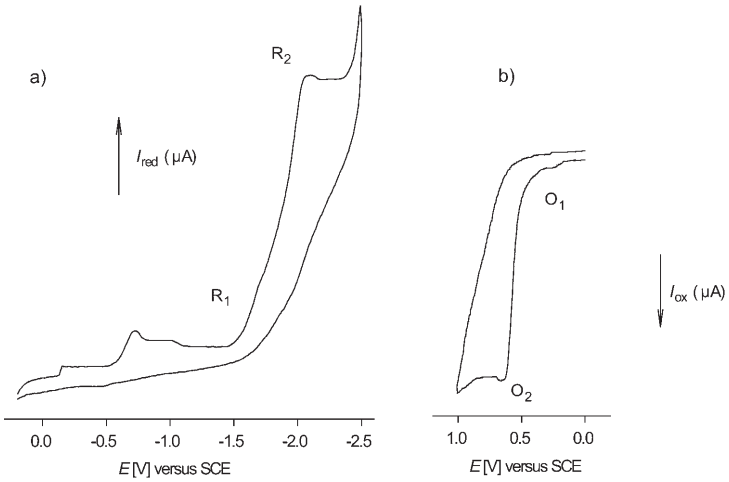


Figure 1. Cyclic voltammetry of [Pd(dppp)IPh] (2 mM) in dmf containing nBu$_4$NBF$_4$ (0.3 M) at a steady gold-disk electrode ($d=0.5$ mm) with a scan rate of 0.2 V s^{-1}. a) Reduction first. b) Oxidation first.

reduction wave R_1 was observed as a shoulder located at less negative potential: $E^p_{R1}=-1.7$ V (Figure 1a). The latter disappeared upon addition of 10 equivalents of nBu$_4$NI, while peak R_2 was conserved. This means that **2b** was the main species reduced at R_2, but being in equilibrium with the minor cationic complex **3**$^+$ reduced at R_1 (Scheme 7). Two oxidation peaks were also observed at +0.25 and +0.7 V when an oxidative potential scan was performed in the range 0–1 V (Figure 1b). Peak O_2 characterizes the oxidation of [Pd(dppp)IPh][15] and peak O_1 the oxidation of I^- released in the equilibrium of Scheme 7, when it is continuously shifted by the electrochemical oxidation of I^-. Thus, even if [Pd(dppp)(dmf)Ph]$^+$ was present at too low a concentration to be observed by ^{31}P NMR spectroscopy, its presence was established voltammetrically by the dual presence of waves O_1 and R_1.

Similarly, two reduction peaks were also observed at $E^p_{R'1}=-1.75$ V (minor) and $E^p_{R'2}=-2.19$ V (major) for the complex [Pd(dppp)(OAc)Ph] (2 mM) in dmf. The reduction current ratio $i_{R'1}/i_{R'2}$ was higher than i_{R1}/i_{R2} obtained for [Pd(dppp)IPh] (2 mM). This finding indicates that the dissociation of AcO^- from [Pd(dppp)(OAc)Ph] (Scheme 8) is easier

$$\underset{\mathbf{2a}}{[Pd(dppp)(OAc)Ph]} \overset{K'_1}{\rightleftharpoons} \underset{\mathbf{3^+}}{[Pd(dppp)(dmf)Ph]^+} + AcO^-$$

Scheme 8.

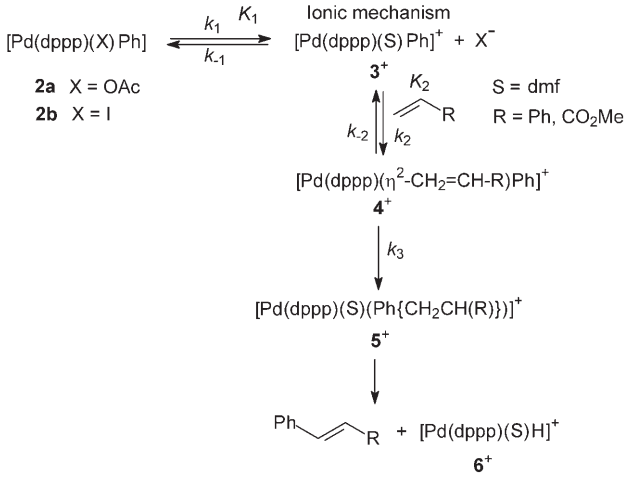
than the dissociation of I^- from [Pd(dppp)IPh] ($K'_1 > K_1$) under the same experimental conditions of concentration and scan rate, in full agreement with the fact that the equilibrium in Scheme 6 lies in favor of [Pd(dppp)IPh] ($K = 0.09 = K_1/K'_1$).

Rate and mechanism of the reaction of [Pd(dppp)(OAc)Ph] (2a) with alkenes (RCH=CH$_2$, R = CO$_2$Me, Ph) in dmf

Reaction of [Pd(dppp)(OAc)Ph] with methyl acrylate; ionic mechanism: The reaction was first monitored by ^{1}H NMR spectroscopy in [D$_6$]acetone by using a slight excess of methyl acrylate in the absence of any base. (*E*)-Methyl cinnamate was generated in 75% yield as the single product (Scheme 9). No branched product was detected, indicative of a good regioselectivity in acetone.

Scheme 9.

The kinetics of the reaction of **2a** with methyl acrylate in dmf (containing 10% [D$_6$]acetone) in the absence of base was followed by ^{31}P NMR spectroscopy by using a capillary of H_3PO_4 (80% in water) as internal standard. The two doublets of **2a** slowly disappeared after addition of excess methyl acrylate. Since the cationic complex [Pd(dppp)(dmf)Ph]$^+$AcO$^-$ had been identified (vide supra), the ionic mechanism of Scheme 10 may be proposed in a first approach. This considers a reversible complexation of the cationic complex **3**$^+$ by the alkene followed by an irreversible carbopalladation step (rate constant k_3). The ensuing complex **5**$^+$ is expected to evolve towards the final products after β-H elimination (as in Scheme 4a).



Scheme 10.

According to this mechanism, the kinetic law for the disappearance of **2a** is given by Equation (1) (X = OAc, R = CO$_2$Me). The rate of the β-H elimination is not relevant when the reaction **4**$^+$→**5**$^+$ is irreversible.

$$\text{rate} = \frac{k_1 k_2 k_3 [\mathbf{2}][\text{CH}_2{=}\text{CHR}]}{k_{-1}k_{-2}[\text{X}^-] + k_{-1}k_3[\text{X}^-] + k_2 k_3 [\text{CH}_2{=}\text{CHR}]} \quad (1)$$

When $k_{-2} \gg k_3$ (fast 2nd equilibrium), Equation (1) can be simplified into Equation (2):

$$\text{rate} = \frac{k_1 k_2 k_3 [\mathbf{2}][\text{CH}_2{=}\text{CHR}]}{k_{-1}k_{-2}[\text{X}^-] + k_2 k_3 [\text{CH}_2{=}\text{CHR}]} \quad (2)$$

Considering the intrinsic fast rate of the equilibrium, **2a** versus **3**$^+$, at low methyl acrylate concentrations $k_{-1}[\text{X}^-] \gg k_2[\text{CH}_2{=}\text{CHR}]$. This gives the simplified Equation (3):

$$\text{rate} = \frac{k_1 k_2 k_3 [\mathbf{2}][\text{CH}_2{=}\text{CHR}]}{k_{-1}k_{-2}[\text{X}^-]} \quad (3)$$

The kinetic law is given in Equation (4) ($x = [\mathbf{2a}]/C_0$; C_0 = initial concentration of **2a**), taking into account the variation of concentration of $X^- = AcO^-$ all along the reaction course. Its integration affords Equation (5):

$$\frac{dx}{dt} = -\frac{K_1 K_2 k_3 [\text{CH}_2{=}\text{CHR}]x}{C_0(1-x)} \quad (4)$$

$$\ln x - x + 1 = -\frac{K_1 K_2 k_3 [\text{CH}_2{=}\text{CHR}]t}{C_0} = -k_{\text{obs}}t \quad (5)$$

Conversely, at higher methyl acrylate concentrations, when $k_{-1}k_{-2}[\text{X}^-] \ll k_2 k_3 [\text{CH}_2{=}\text{CHR}]$, the simplified kinetic law in Equation (6) is obtained whose integration gives Equation (7). The rate-limiting step will thus be the dissociation of **2a** to **3**$^+$, independent of the methyl acrylate concentration.

$$\frac{dx}{dt} = -k_1 x \quad (6)$$

$$\ln x = -k_1 t \quad (7)$$

At low methyl acrylate concentrations (up to 1.5 M), the plot of $\ln x - x + 1$ against time were linear (Figure S1 in the Supporting Information), as expressed in Equation (5). The observed rate constant k_{obs}, determined from the slope of the straight line, varied linearly with methyl acrylate concentration (Figure 2a), attesting to a first-order reaction for the methyl acrylate as predicted in Equation (5). Conversely, at higher methyl acrylate concentrations, $\ln x$ was found to vary linearly with time (Figure 2a). The observed rate constant k_{obs} did not depend on the methyl acrylate concentration as predicted in Equation (7). $K_1K_2k_3$ was calculated from the slope of the straight line obtained at low methyl acrylate concentration and k_1 from the limiting value of k_{obs} in Figure 2a (Table 1).

The kinetic data thus agree with the ionic mechanism proposed in Scheme 10. For confirmation, the effects of AcO^-

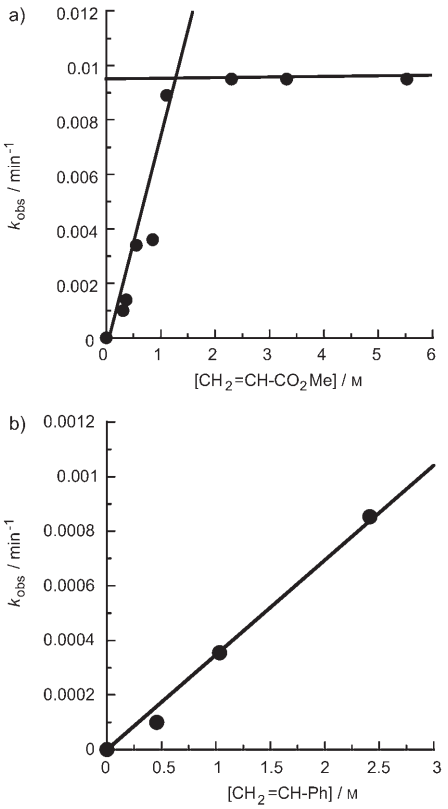


Figure 2. Kinetics of the reaction of [Pd(dppp)(OAc)Ph] (**2a**) in dmf at 25 °C with a) methyl acrylate and b) styrene. Determination of the reaction order in alkenes: plot of k_{obs} against alkene concentration.

Table 1. Rate constants of the reaction of [Pd(dppp)XPh] (X = I, OAc) with alkenes (see Schemes 10 and 11 for the definitions of k_1 and $K_1K_2k_3$).

	k_1 [s^{-1}]	Methyl acrylate $K_1K_2k_3$ [s^{-1}]	Styrene $K_1K_2k_3$ [s^{-1}]
[Pd(dppp)(OAc)Ph]	$1.6(\pm0.1)\times10^{-4}$	$1.5(\pm0.1)\times10^{-6}$	$6.6(\pm0.1)\times10^{-8}$
[Pd(dppp)IPh]	$1.1(\pm0.1)\times10^{-4}$	$1.0(\pm0.1)\times10^{-6}$	$3.8(\pm0.1)\times10^{-8}$

and ionic strength were probed. The effect of the ionic strength was first investigated by monitoring the reaction of [Pd(dppp)(OAc)Ph] (C_0 = 12.2 mM) with various amounts of methyl acrylate, in the presence of increasing amounts of nBu$_4$NBF$_4$. The reaction went faster upon increasing the ionic strength (Figure 3). The values of $K_1K_2k_3$ increased with increasing ionic strength (Figure 3a–c), as did those of k_1 (Figure 3a′–c′). As expected, the dissociation of **2a** to **3**$^+$ was favored at high ionic strength.

According to the ionic mechanism proposed in Scheme 10, a decelerating effect of AcO$^-$ (introduced as nBu$_4$NOAc) on the reactivity of [Pd(dppp)(OAc)Ph] should be observed [Eq. (3), with X = OAc]. However, this effect should be partly compensated by the accelerating effect of the ionic strength due to the addition of ionic species nBu$_4$N$^+$ and AcO$^-$ (free ions in dmf). The value of k_{obs} was determined for different methyl acrylate concentrations in the presence of various amounts of nBu$_4$NOAc. The plot of

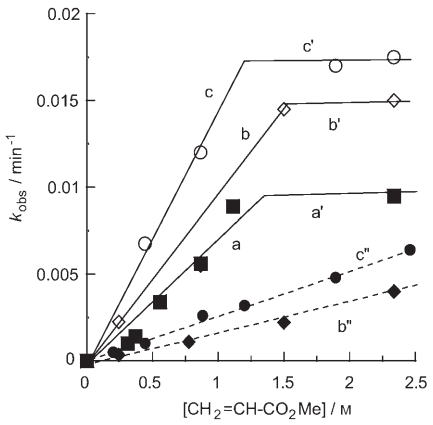


Figure 3. Kinetics of the reaction of [Pd(dppp)(OAc)Ph] (**2a**) (C_0 = 12.2 mM) with methyl acrylate in dmf at 25 °C. Effect of ionic strength and acetate ions: plot of k_{obs} versus methyl acrylate concentration in the absence of salts (■); in the presence of [nBu$_4$NBF$_4$] = 244 mM (○); [nBu$_4$NBF$_4$] = 122 mM (◇); [nBu$_4$NOAc] = 244 mM (●); [nBu$_4$NOAc] = 122 mM (◆).

k_{obs} against methyl acrylate concentration was linear for each concentration of nBu$_4$NOAc (Figure 3b″,c″), but the saturating effect could not be observed in the concentration range investigated here. When comparing the slope of the straight lines obtained in the presence of nBu$_4$NOAc and nBu$_4$NBF$_4$ at the same concentration, that is, at identical ionic strength, one observes that the reaction was slower in the presence of AcO$^-$ (Figure 3). Consequently, a specific effect of the acetate ions is observed, the reaction of [Pd(dppp)(OAc)Ph] with methyl acrylate being slower in the presence of AcO$^-$, in agreement with the ionic mechanism of Scheme 10.[16]

Reaction of [Pd(dppp)(OAc)Ph] with styrene; ionic mechanism: This reaction has been investigated by Åkermark et al. in dmf but without any kinetic data.[8] It gives a mixture of the branched CH$_2$=CPh$_2$ and linear PhCH=CHPh products in the ratio 18:82. The kinetics of the reaction of [Pd(dppp)(OAc)Ph] (**2a**; C_0 = 11.5 mM) with styrene in dmf was monitored by ^{31}P NMR spectroscopy, as for methyl acrylate. The reaction was considerably slower than that involving methyl acrylate at identical concentrations. The reaction was first order in styrene (Figure 2b) and did not display any saturating effect all along the investigated styrene concentration range (up to 2.3 M). The reaction was thus never limited by the dissociation of **2a** to **3**$^+$.[17] An accelerating effect was observed when performing the reaction at high ionic strength.[18] No reaction was observed in the presence of 10 equivalents of nBu$_4$NOAc, which means that the decelerating effect of AcO$^-$ was now considerably higher than the accelerating effect due to its ionic strength. All these results again support the involvement of the ionic mechanism (Scheme 10) for the reaction of [Pd(dppp)(OAc)Ph] with styrene, which proceeds via [Pd(dppp)(dmf)Ph]$^+$. $K_1K_2k_3$ was determined from the slope of the straight line in Figure 2b (Equation (5), Table 1).

Rate and mechanism of the reaction of [Pd(dppp)IPh] (2b) with alkenes (RCH=CH$_2$; R = CO$_2$Me, Ph) in dmf

Reaction of [Pd(dppp)IPh] with styrene; ionic mechanism: This reaction has also been investigated by Åkermark et al. but without any kinetic data.[8] The branched CH_2=CPh_2 and linear PhCH=CHPh products were formed in the ratio 20:80. The kinetics of the reaction of **2b** with styrene were monitored by ^{31}P NMR spectroscopy. The reaction was first order in styrene (Figure 4b) in agreement with Equation (5).

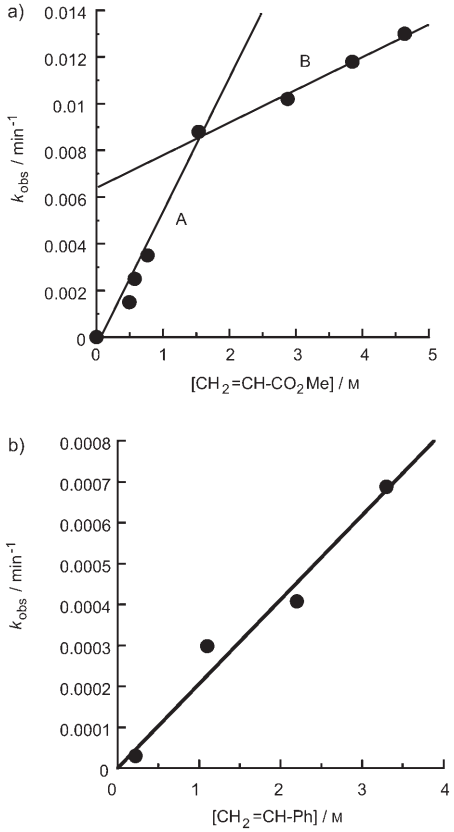


Figure 4. Kinetics of the reaction of [Pd(dppp)IPh] (**2b**) in dmf at 25 °C with a) methyl acrylate and b) styrene. Determination of the reaction order in alkenes: plot of k_{obs} against alkene concentration.

The reaction was highly accelerated at high ionic strength (by a factor of 100 in the presence of 0.3 M nBu$_4$NBF$_4$) but slower in the presence of I$^-$ (10 equiv introduced as nBu$_4$NI; Figure S2 in Supporting Information), attesting to the involvement of [Pd(dppp)(dmf)Ph]$^+$ as the main reactive intermediate (Scheme 10). $K_1K_2k_3$ was determined from the slope of the straight line of Figure 4b (Table 1).

Reaction of [Pd(dppp)IPh] with methyl acrylate; ionic and neutral mechanisms: The reaction of [Pd(dppp)IPh] (**2b**) with methyl acrylate *in the absence of base* yielded (*E*)-methyl cinnamate in 89% yield in acetone. The kinetics of the reaction were investigated in dmf without any base by ^{31}P NMR spectroscopy. The plot of k_{obs} versus methyl acrylate concentration is shown in Figure 4a. A straight line (A) was obtained at low methyl acrylate concentrations (<1.5 M). At higher methyl acrylate concentrations, a progressive saturation was observed (line B in Figure 4a), although less sharp than in the case of [Pd(dppp)(OAc)Ph] (compare Figure 2a). However, the saturation limit that would deliver the value of k_1 (the rate constant of the dissociation of [Pd(dppp)IPh] into [Pd(dppp)(dmf)Ph]$^+$ and I$^-$ in the pure ionic mechanism of Scheme 10) has to be larger than 2.3×10^{-4} s^{-1} (Figure 4a). Such a value would be higher than the corresponding one, $k_1=1.6\times10^{-4}$ s^{-1}, determined for the dissociation of [Pd(dppp)(OAc)Ph] (Table 1). This result is inconsistent, as [Pd(dppp)IPh] is less easily dissociated than [Pd(dppp)(OAc)Ph] (vide supra). Accordingly, the hypothesis concerning a saturating effect limited by k_1 cannot be retained. We thus need to consider that the would-be saturating effect is unobservable because another mechanism overtakes it. In other words, we need to consider two competing mechanisms occurring at low methyl acrylate concentrations, one being the ionic one. When the ionic mechanism reaches its saturation limit, the second slower one shows up. Within this framework, the rate law of the second mechanism is given by the straight line observed at high methyl acrylate concentrations (line B in Figure 4a). It ensues that the slope of line A in Figure 4a represents the sum of the rates of the two competing mechanisms.

To test for this rationalization, the reaction of **2b** (12.2 mM) with methyl acrylate was monitored in the presence of excess I$^-$ (nBu$_4$NI, 122 mM). A first-order reaction for methyl acrylate was found all along the concentration range investigated here (0–4 M, Figure S3a in the Supporting Information). At identical methyl acrylate concentrations, the reaction was slower ($k_{app}=4.3\times10^{-5}$ M^{-1}s^{-1}) than that performed in the presence of nBu$_4$NBF$_4$ (122 mM) at the same ionic strength ($k_{app}=2.5\times10^{-4}$ M^{-1}s^{-1}, Figure S3b in the Supporting Information), and also slower than the one performed in the absence of I$^-$(k_{app}=9.3×1^{-5} M^{-1}s^{-1}, line A in Figure 4a). These results attest to a specific effect of I$^-$, leading to a deceleration much more important than the acceleration due to its ionic strength.

The reaction of **2b** ($C_0=12.2$ mM) with methyl acrylate (2.44 M) was then monitored in the presence of various amounts of I$^-$ (up to 0.3 M). The higher the I$^-$ concentration, the slower the reaction. The plot of k_{obs} versus the reciprocal of the I$^-$ concentration was linear but with a positive intercept (Figure 5). A purely ionic mechanism would have given a zero intercept [Eq. (3)]. This result confirms that the mechanism is a mixture of a neutral mechanism (I$^-$ independent) and an ionic mechanism (I$^-$ dependent; Scheme 11). Both [Pd(dppp)(dmf)Ph]$^+$ and [Pd(dppp)IPh] react competitively, although the cationic complex is more reactive than the neutral one when its concentration is sufficient, namely, at lower methyl acrylate and I$^-$ concentrations.

Considering that the two η^2-CH=CHR ligated compounds **4b** and **4**$^+$ are in a steady state, the rate law corresponding to the mixed mechanism of Scheme 11 is given by Equa-

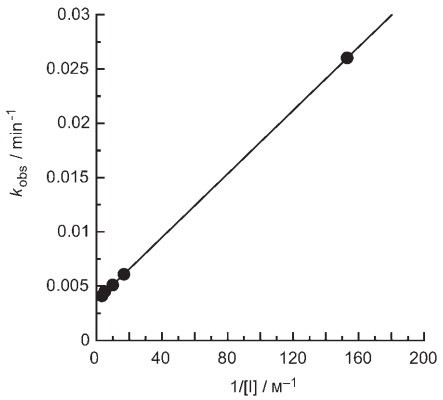
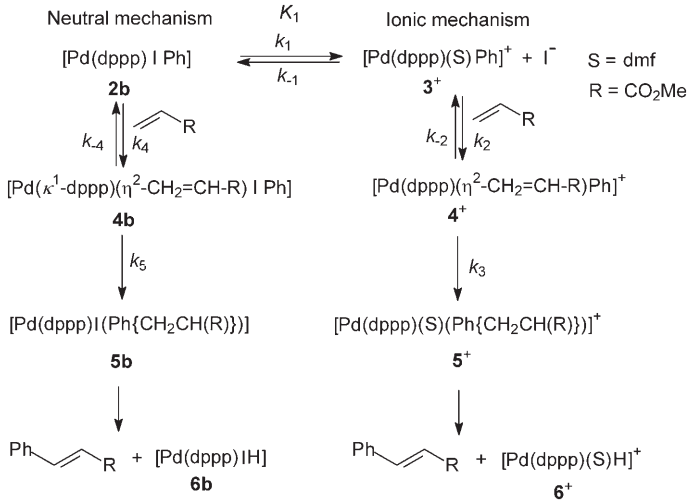


Figure 5. Effect of iodide ions on the kinetics of the reaction of [Pd(dppp)IPh] (**2b**) ($C_0 = 12.2$ mM) with methyl acrylate (2.44 M) in dmf at 25 °C. Plot of k_{obs} versus 1/[I$^-$].



Scheme 11.

tion (8) (R = CO_2Me, X = I), in which the first term is the contribution of the neutral mechanism and the second one that of the ionic mechanism.

$$k_{obs} = \frac{k_4 k_5 [CH_2{=}CHR]}{k_{-4} + k_5} + \frac{k_1 k_2 k_3 [CH_2{=}CHR]}{k_{-1} k_{-2} [X^-] + k_2 k_3 [CH_2{=}CHR]} \quad (8)$$

At high I$^-$ concentrations, $k_{-1}k_{-2}[I^-] \gg k_2k_3[CH_2{=}CHCO_2Et]$, Equation (8) simplifies into Equation (9):

$$k_{obs} = \frac{k_4 k_5 [CH_2{=}CHR]}{k_{-4} + k_5} + \frac{k_1 k_2 k_3 [CH_2{=}CHR]}{k_{-1} k_{-2} [X^-]} \quad (9)$$

The intercept of the straight line of Figure 5 gives the value of $k_4k_5/(k_{-4}+k_5) = 2.5 \times 10^{-5}$ M^{-1}s^{-1} (dmf, 25 °C), whereas the slope gives the value of $K_1K_2k_3 = 1 \times 10^{-6}$ s^{-1} (dmf, 25 °C).

Coming back to Figure 4a, in which no I$^-$ had been added and at high methyl acrylate concentrations, Equation (8) gives Equation (10) upon considering that $k_{-1}k_{-2}[I^-] \ll k_2k_3[CH_2{=}CHCO_2Me]$.

$$k_{obs} = \frac{k_4 k_5 [CH_2{=}CHR]}{k_{-4} + k_5} + k_1 \quad (10)$$

This corresponds to a saturation limit for the ionic mechanism, while the neutral one proceeds. The value of $k_1 = 6.5 \times 10^{-3}$ min^{-1} (dmf, 25 °C) is calculated from the intercept of line B of Figure 4a, while the slope gives $k_4k_5/(k_{-4}+k_5) = 2.3 \times 10^{-5}$ M^{-1}s^{-1} (dmf, 25 °C), a value which is close to that determined above from Figure 5 (2.5×10^{-5} M^{-1}s^{-1}).[19]

Therefore, albeit the results obtained under the different conditions of Figures 4a and 5 are independent, they are fully consistent. Furthermore, within this dual-mechanism framework, $k_1 = 1.1 \times 10^{-4}$ s^{-1} is found for [Pd(dppp)IPh]. This value is about twice as small as that for [Pd(dppp)(OAc)Ph] (Table 1), which agrees with the fact that the dissociation of I$^-$ is more difficult than that of AcO$^-$ in [Pd(dppp)XPh]. These results are extremely coherent and validate the formulation in Scheme 11, that is, a parallel involvement of the ionic and neutral mechanisms in the reaction of methyl acrylate. The mechanism of the reaction of [Pd(dppp)IPh] with alkenes is then substrate dependent.

Reactivity of [Pd(dppp){dppp(O)}Ph]$^+$ with methyl acrylate in dmf: The complex [Pd(dppp){dppp(O)}Ph]$^+$ (**1**) was generated in situ in the reaction of PhI (1 equiv) with the Pd^0 complex formed from $Pd(OAc)_2$, dppp (2 equiv), H_2O (20 equiv), and NEt_3 (30 equiv), as reported in our previous work.[10a] Its reaction with methyl acrylate was monitored by ^{31}P NMR spectroscopy (Supporting Information) and was extremely slow, even in the presence of a large excess of alkene (500 equiv). The signals of [Pd(dppp)IPh] were then observed at long time intervals due to the slow reaction of I$^-$ released during the oxidative addition of PhI with [Pd(dppp){dppp(O)}Ph]$^+$ (Scheme 5). Consequently, the kinetics of the reaction of **1** with methyl acrylate or styrene were too slow to be monitored precisely.

Nevertheless, such results emphasize the role of I$^-$ or AcO$^-$ ions. By their parallel reaction with [Pd(dppp){dppp(O)}Ph]$^+$, they generate [Pd(dppp)IPh] or [Pd(dppp)(OAc)Ph], respectively, which then react competitively with alkenes. [Pd(dppp){dppp(O)}Ph]$^+$ is thus a transient species, as its lifetime is expected to be short in the presence of a large number of I$^-$ or AcO$^-$ ions (as in catalytic reactions). Yet, it cannot be considered as truly reactive in the carbopalladation step.

Conclusion

In Heck reactions performed from iodobenzene and catalyzed by $Pd(OAc)_2$ associated to two equivalents of dppp, the complex [Pd(dppp){dppp(O)}Ph]$^+$ is generated in the oxidative addition of PhI with [Pd^0(dppp)(OAc)]$^-$ in dmf. [Pd(dppp){dppp(O)}Ph]$^+$ is not very reactive with alkenes,

such as those investigated here (styrene or methyl acrylate). However, it rapidly becomes a transient species under effective catalytic conditions. Indeed, its reaction with I^- ions which are released in the catalytic reaction, or with AcO^- ions used as a base, generates [Pd(dppp)IPh] and [Pd(dppp)(OAc)Ph], respectively. [Pd(dppp)(OAc)Ph] reacts with styrene and methyl acrylate exclusively by an ionic mechanism, that is, via the cationic complex $[Pd(dppp)(dmf)Ph]^+$ formed by dissociation of AcO^- (Scheme 10). The reaction of [Pd(dppp)IPh] is more complex and substrate dependent, due to the larger stability of this species vis-à-vis its ionic dissociation. It reacts with styrene exclusively by the ionic mechanism via $[Pd(dppp)(dmf)Ph]^+$ (Scheme 10). As far as methyl acrylate is concerned, the neutral and ionic mechanisms compete in parallel (Scheme 11). Clearly, $[Pd(dppp)(dmf)Ph]^+$ is more reactive than [Pd(dppp)IPh], but its intrinsic higher energy maintains it at concentrations that are too low to allow it to compete efficiently at high I^- or methyl acrylate concentrations.

The following reactivity orders have been established:- whatever the complex [Pd(dppp)XPh] (X = I, OAc): CH_2=$CHCO_2Me$ > CH_2=CHPh; whatever the alkene: $[Pd(dppp)(dmf)Ph]^+$ > [Pd(dppp)XPh] (X = OAc, I) ≫ $[Pd(dppp)\{dppp(O)\}Ph]^+$

All these results differ from the generally postulated mechanism, which mostly proposes a neutral mechanism from [Pd(dppp)XPh] (X = I). Moreover, it has been established in this work that [Pd(dppp)IPh] and [Pd(dppp)(OAc)Ph] are involved in a dynamic equilibrium with the anions I^- and AcO^-. In a real Heck reaction, the respective anion concentrations will vary in the course of the catalytic reaction and consequently the concentration of the reactive complex $[Pd(dppp)(dmf)Ph]^+$ will also vary and decrease all along the catalytic reaction. However, an antagonistic effect is then observed between the specific inhibiting effect of I^- and AcO^- and the accelerating effect due to increasing ionic strength.

As evidenced by Åkermark et al., the solvent may also play an important role through its dissociation properties which favor the ionic process.[8] Heck reactions performed from an electron-rich alkene usually give branched alkenes under the conditions of the ionic mechanism, that is, starting from aryl triflates or aryl iodides in the presence of Ag^+ or Tl^+ salts, which both generate $[Pd(dppp)(dmf)(Ar)]^+$ quantitatively.[1e,2f–k,4] Xiao et al. have reported that a Heck reaction catalyzed by $Pd(OAc)_2$ associated with dppp and performed from an electron-rich alkene and ArI (without any iodide scavenger, that is, under the conditions of the neutral "textbook" mechanism of Scheme 2 gave a mixture of branched and linear products in dmf, whereas the branched product was exclusively produced in ionic liquids.[20] This result emphasizes concretely the synthetic significance of the results established in this work: the cationic complex $[Pd(dppp)(S)Ph]^+$ is the most intrinsically reactive complex, and its overall role is larger at high ionic strength (as in ionic liquids) and affords the regioselectivity of the ionic mechanism observed with electron-rich alkenes.[1e,2f–k]

All these kinetic results, associated with a previous work on the kinetics of the oxidative addition to PhI,[10a] established that for identical concentrations of PhI and alkenes (styrene, methyl acrylate), the oxidative addition is much faster than the so-called carbopalladation step (reaction of alkenes with [Pd(dppp)X(Ar)] complexes), which is the rate-determining step of the catalytic reaction and introduces the main mechanistic complexities of the overall Heck reaction.

Experimental Section

General: ^{31}P NMR spectra were recorded on a Bruker spectrometer (101.3 MHz) in dmf containing 10% $[D_6]$acetone. A capillary tube containing H_3PO_4 (85% in water) was introduced into the NMR tube to serve as an internal standard for the kinetic studies. ^1H NMR spectra were recorded on a Bruker spectrometer (250 MHz). Cyclic voltammetry was performed at gold disk electrodes with a homemade potentiostat and a waveform generator (Tacussel GSTP4). The cyclic voltammograms were recorded on a Nicolet 301 oscilloscope.

Chemicals: dmf was distilled from calcium hydride under vacuum and kept under argon. $Pd(OAc)_2$, styrene, methyl acrylate, PhI, nBu$_4$NI, nBu$_4$NOAc, nBu$_4$NBF$_4$, and the ligand dppp were commercial.

Synthesis of [Pd(dppp)(OAc)Ph] (2a): This compound was synthesized from [Pd(dppp)IPh] according to the literature.[8] ^{31}P NMR (101.3 MHz, dmf + $[D_6]$acetone, H_3PO_4): $\delta = 18.91$ (d, $^2J(P,P) = 48.5$ Hz), −4.18 ppm (d, $^2J(P,P) = 48.5$ Hz); ^{31}P NMR (101.3 MHz, $[D_6]$acetone, H_3PO_4): $\delta = 19.40$ (d, $^2J(P,P) = 48.5$ Hz), −3.70 ppm (d, $^2J(P,P) = 48.5$ Hz); FAB MS: m/z = 595 [M^+−OAc], 518 [M^+−OAc−Ph].

Synthesis of [Pd(dppp)IPh] (2b): This compound was synthesized according to a published procedure.[8] A slow crystallization from acetone gave orange crystals (yield: 75%). ^{31}P NMR (101.3 MHz, $[D_6]$acetone, H_3PO_4): $\delta = 11.94$ (d, $^2J(P,P) = 53.6$ Hz), −9.05 ppm (d, $^2J(P,P) = 53.6$ Hz); ^{31}P NMR (101.3 MHz, dmf + 10% $[D_6]$acetone, H_3PO_4): $\delta = 12.11$ (d, $^2J(P,P) = 53.6$ Hz), −8.88 ppm (d, $^2J(P,P) = 53.6$ Hz); UV: λ_{max} (ε) = 334 (1800) nm; FAB MS: m/z = 653 [M^+−I + acetone], 518 [M^+−I].

Reaction of [Pd(dppp)(OAc)Ph] (2a) with methyl acrylate: The reaction was performed in a Schlenk tube under argon. Methyl acrylate (1 μL, 11.2 μmol) was added at room temperature to a solution of **2a** (2.3 mg, 3.4 μmol) in $[D_6]$acetone (400 μL). The yellow solution turned progressively red. The ^1H NMR spectra showed the progressive disappearance of the signal of the Ph group linked to the Pd(II) center of **2a** and those of the methyl acrylate to afford the signals of (*E*)-methyl cinnamate similar to those of an authentic sample. After one month, a black solution was obtained, **2a** was no longer observed, and (*E*)-methyl cinnamate was exclusively formed without any (*Z*)-methyl cinnamate or branched isomethyl cinnamate. The ^{31}P NMR spectrum revealed the signal of the hemioxide dppp(O) at 29.9 ppm. The excess methyl acrylate was eliminated under vacuum. 1,1,2,2-Tetrachloroethane (1μL, 9.3 μmol) was then added as an internal standard to determine the amount of (*E*)-methyl cinnamate formed in the reaction (75% yield).

Reaction of [Pd(dppp)IPh] (2b) with methyl acrylate: The reaction was performed as above starting from a solution of **2b** (5 mg, 6.9 μmol). After addition of methyl acrylate (1 μL, 11.5 μmol), the yellow solution of **2b** turned progressively red. After one month and workup, (*E*)-methyl cinnamate was formed in 89% yield.

Electrochemical setup and procedure for cyclic voltammetry: Experiments were carried out in a three-electrode thermostated cell connected to a Schlenk line. The counter electrode was a platinum wire of approximately 1 cm^2 apparent surface area. The reference was a SCE separated from the solution by a bridge filled with dmf (3 mL) containing nBu$_4$NBF$_4$ (0.3 M). The working electrode was a gold-disk electrode (d = 0.5 mm).

Kinetics of the reaction of [Pd(dppp)(OAc)Ph] (2a) with methyl acrylate as monitored by ^{31}P NMR spectroscopy: Complex **2a** (4.8 mg, 7.3 μmol)

was introduced into an NMR tube containing dmf (400 μL) and [D_6]acetone (200 μL). A capillary of H_3PO_4 was then introduced as an internal standard. A known amount of methyl acrylate was added and the kinetics were followed by ^{31}P NMR spectroscopy, until total conversion, by the decrease of the two doublets of **2a** at −4.18 and 18.91 ppm whose total integration was compared to that of H_3PO_4. In other experiments, known amounts of nBu$_4$NBF$_4$ were added before the methyl acrylate to probe the effect of the ionic strength on the kinetics. In addition, known amounts of nBu$_4$NOAc were added before the methyl acrylate to probe the effect of acetate ions on the kinetics.

Kinetics of the reaction of [Pd(dppp)IPh] (2b) with methyl acrylate as monitored by ^{31}P NMR spectroscopy: The reaction was performed as above by starting from **2b** (5 mg, 6.9 μmol) and various amounts of methyl acrylate. nBu$_4$NBF$_4$ was added before the methyl acrylate to probe the effect of the ionic strength on the kinetics. In other experiments, known amounts nBu$_4$NI were added before the methyl acrylate to probe the effect of iodide ions on the kinetics.

Kinetics of the reaction of [Pd(dppp)(OAc)Ph] (2a) with styrene as monitored by ^{31}P NMR spectroscopy: The reaction was performed as above by starting from **2a** (4.5 mg, 6.9 μmol) and various amounts of styrene. nBu$_4$NBF$_4$ was added before the styrene to probe the effect of the ionic strength on the kinetics. In other experiments, known amounts nBu$_4$NOAc were added before the styrene to probe the effect of acetate ions on the kinetics.

Kinetics of the reaction of [Pd(dppp){dppp(O)}Ph]$^+$ with styrene or methyl acrylate as monitored by ^{31}P NMR spectroscopy: NEt$_3$ (50 μL, 0.36 mmol), water (5 μL, 0.24 mmol), dppp (10 mg, 24 μmol), and Pd(OAc)$_2$ (2.7 mg, 12 μmol) were added successively to dmf (500 μL). After 30 min, which corresponds to the quantitative formation of [Pd^0(dppp)(OAc)]$^-$, PhI (1.5 μL, 12 μmol) was added followed by [D_6]acetone (100 μL). The complex [Pd(dppp){dppp(O)}Ph]$^+$ generated in the oxidative addition was identified by ^{31}P NMR spectroscopy as a unique complex (Supporting Information).[10a] A capillary of H_3PO_4 was introduced into the NMR tube followed by methyl acrylate (76.8 μL, 0.42 mmol). The reaction was monitored by ^{31}P NMR spectroscopy.

Acknowledgements

This work was supported in part by the Centre National de la Recherche Scientifique (UMR CNRS-ENS-UPMC 8640) and the Ministère de la Recherche (Ecole Normale Supérieure). Johnson Matthey is thanked for a generous loan of palladium salts. AFIRST (Association Franco-Israélienne pour la Recherche Scientifique et la Technologie) is thanked for supporting F.L. with a postdoctoral grant (991 MAE CCF5).

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[17] The minimum concentration of styrene beyond which the reaction would be limited by the dissociation of [Pd(dppp)(OAc)Ph] can be estimated from the transition between the limits in Equations (4) and (6): $[\text{styrene}]/[AcO^-] = k_1/K_1K_2k_3$. From the values of k_1 (Table 1) and $K_1K_2k_3$ (see below), and the fact that [AcO$^-$] cannot

exceed C_0, this equality imposes the condition that at least 2500 equivalents of styrene ($\approx$30 M) would be required to observe the saturation effect.

[18] The half reaction time varied from $t_{1/2}$ = 1030 to 417 min when the reaction of [Pd(dppp)(OAc)Ph] (1.15 mM) with styrene (1.15 M) was performed in the presence of nBu$_4$NBF$_4$ (0.26 M).

[19] Conversely, when the methyl acrylate concentration is lower under the conditions of Figure 4a (line A), the rate law is given by Equation (9). It predicts a nonlinear dependence of k_{obs} versus [CH_2=CHR], because the term [X^-] varies. However, this term is of the order of C_0 = 12.2 mM in the experimental conditions of Figure 4a. Thus, by using the values of $k_4k_5/(k_{-4}+k_5)$ and $K_1K_2k_3$ determined above, it follows that the mean value of k_{obs} at low methyl acrylate concentrations is $k_{obs}(min^{-1}) = 5\times10^{-3}\times$[$CH_2$=CHR], namely, exactly in the range observed for line A in Figure 4a.

[20] a) L. J. Xu, W. P. Chen, J. Ross, J. L. Xiao, *Org. Lett.* **2001**, *3*, 295–297; b) J. Mo, L. Xu, J. Xiao, *J. Am. Chem. Soc.* **2005**, *127*, 751–760.

Received: February 3, 2006
Published online: November 28, 2006

