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Decelerating Effect of Alkenes in the Oxidative Addition of Phenyl Iodide to Palladium(0) Complexes in Heck Reactions

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In DMF, the oxidative addition of PhI to $Pd^0(PPh_3)_4$ or to the anionic $Pd^0(PPh_3)_3(OAc)^-$ is slower in the presence of an alkene (styrene, methyl acrylate). Indeed, the concentration of the reactive $Pd^0(PPh_3)_2$ or $Pd^0(PPh_3)_2(OAc)^-$ complex decreases because of its coordination to the alkene to form the unreactive $(\eta^2\text{-}CH_2{=}CHR)Pd^0(PPh_3)_2$ (R = Ph, CO_2Me) or $(\eta^2\text{-}CH_2{=}CHPh)Pd^0(PPh_3)_2(OAc)^-$, respectively. As already evidenced in palladium-catalyzed Stille reactions, this work establishes that, in palladium-catalyzed Heck reactions as well, the nucleophile plays a role in the kinetics of the oxidative addition (decelerating effect), as soon as it may coordinate Pd^0 complexes. This is an essential observation, in view of the general belief that the nucleophile enters the catalytic cycle only at the stage of the attack on the aryl−Pd^{II} complex formed in the oxidative addition. Whenever the oxidative addition is not rate determining, the decelerating effect of the alkene on this reaction is in favor of a higher efficiency of the catalytic cycle.

Introduction

In palladium-catalyzed Stille reactions (eq 1)[1] or Heck reactions (eq 2),[2] the first step of the catalytic cycle is an oxidative addition of the aryl halide to a Pd^0 complex, which gives an aryl−Pd^{II} complex. The nucleophile is

$$ArX + CH_2{=}CHSnBu_3 \xrightarrow{[Pd]} ArCH{=}CH_2 + XSnBu_3 \quad (1)$$

$$ArX + CH_2{=}CHR + NEt_3 \xrightarrow{[Pd]} ArCH{=}CHR + Et_3NH^+X^- \quad (2)$$

supposed to enter the catalytic cycle only after this reaction, by reacting with the aryl−Pd^{II} complex in a transmetalation step in Stille reactions[1,3] or a carbopalladation step[2] in Heck reactions. Further evolution of the ensuing intermediates gives the reaction product(s) and regenerates the active Pd^0 catalyst.

In a Stille reaction between PhI and a nucleophile such as tributyl(vinyl)tin (eq 1), catalyzed by $Pd^0(dba)_2$ (dba = *trans*,*trans*-dibenzylideneacetone) associated with 2 equiv of $AsPh_3$, we previously established that the nucleophile plays a role at the level of the first step: i.e., in the oxidative addition of PhI to the Pd^0 catalyst.[4] Indeed, the overall oxidative addition is slower in the presence of the nucleophile because the concentration of the active complex $Pd^0(AsPh_3)_2$ decreases, due to its reversible coordination by the C=C bond of the nucleophile to form the unreactive complex: $(\eta^2\text{-}CH_2{=}CHSnBu_3)Pd^0(AsPh_3)_2$ (Scheme 1).[4]

In a Heck reaction between PhOTf and $CH_2{=}CH{-}CO_2Me$ (eq 2), catalyzed by $Pd^0(dba)_2$ associated with 1 equiv of dppf (dppf = 1,1′-bis(diphenylphosphino)ferrocene), the complex $(\eta^2\text{-}CH_2{=}CHCO_2Me)Pd^0(dppf)$ has been isolated in the course of the reaction and found to be the reactive species in the oxidative addition to aryl triflates or iodides (Scheme 2).[5]The oxidative addition was faster in the presence of Eu^{3+} cations, which coordinate the methyl acrylate, thus increasing the concentration of the more reactive $Pd^0(dppf)$ complex (Scheme 2).[5] Once again, the nucleophile plays a role in the oxidative addition, leading to a decelerating effect due to its complexation to the more reactive Pd^0 complex.

Such kinetics investigations[4,5] could be successfully achieved because they were carried out under experimental conditions such as oxidative addition and the transmetalation (Stille reaction) and carbopalladation (Heck reaction) were disconnected. Indeed, the oxidative addition, even if slowed by the presence of the nucleophile, remained faster than the nucleophilic attack on the aryl−Pd^{II} complex. Under such conditions, the Pd^0 catalyst was recycled only after the slow nucleophilic attack, viz., on a time scale considerably longer than that required to complete the oxidative addition. Thus, the kinetics of the oxidative addition could be investi-

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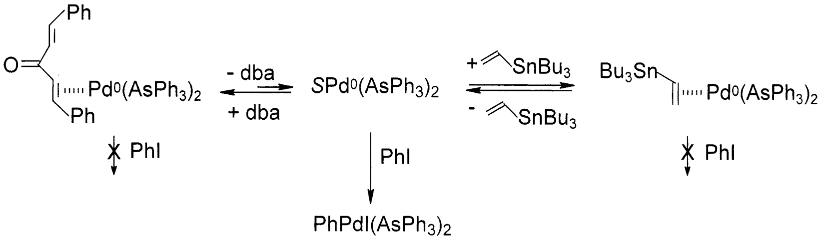
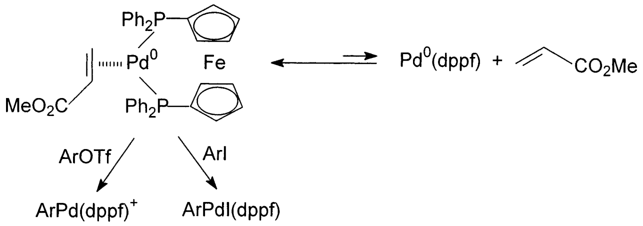
Scheme 1



Scheme 2



Scheme 3. Mechanism of the Oxidative Addition of PhI to $Pd^0(PPh_3)_4$ (S = Solvent)

$$Pd^0(PPh_3)_4 \rightleftharpoons Pd^0(PPh_3)_3 + PPh_3 \qquad (4)$$

$$Pd^0(PPh_3)_3 \overset{K_1}{\rightleftharpoons} SPd^0(PPh_3)_2 + PPh_3 \qquad (5)$$

$$SPd^0(PPh_3)_2 + PhI \xrightarrow{k} PhPdI(PPh_3)_2 \qquad (6)$$

Overall reaction:

$$Pd^0(PPh_3)_4 + PhI \xrightarrow{k_{app}} PhPdI(PPh_3)_2 + 2PPh_3 \qquad (7)$$

gated without kinetic interference, due to the follow-up reactions of the catalytic cycle.

We report herein further investigations, which generalize the role played by the nucleophile in the kinetics of oxidative additions, leading to a decelerating effect as soon as the nucleophile can coordinate the active low ligated Pd^0 moiety. The effect of two representative coordinating nucleophiles, styrene and methyl acrylate, has been investigated in the oxidative addition of PhI to $Pd^0(PPh_3)_4$ or to $Pd^0(PPh_3)_3(OAc)^-$, the latter Pd^0 precursor being an effective catalyst in Heck reactions (eq 3).[2d]

$$PhI + CH_2{=}CHPh + NEt_3 \xrightarrow{[Pd]} PhCH{=}CHPh + Et_3NH^+I^- \quad (3)$$

Results and Discussion

Oxidative Addition of PhI to $Pd^0(PPh_3)_4$ in the Presence of Styrene, in DMF. The oxidative addition of PhI to $Pd^0(PPh_3)_4$ gives the *trans*-$PhPdI(PPh_3)_2$ complex[6] (Scheme 3). This species does not react with styrene in DMF at 25 °C to form stilbene, the would-be final compound of a Heck reaction.[7c,2d] Consequently, the Pd^0 catalyst is not recycled and the kinetics of the oxidative addition of PhI can be investigated in the presence of styrene without any perturbation caused by the recycling of the Pd^0 complex.

The kinetics of the oxidative addition of PhI (2 mM) to $Pd^0(PPh_3)_4$ (2 mM) in DMF (containing n-Bu_4NBF_4, 0.3 M) was first investigated in the absence of any styrene (Scheme 3, eq 7). It was monitored analytically using amperometry at a rotating disk electrode, polarized at +0.2 V vs SCE, i.e., on the oxidation wave of $Pd^0(PPh_3)_3$, the major complex formed in solution from $Pd^0(PPh_3)_4$ (eqs 4 and 5).[8] The decay of the oxidation current (proportional to the Pd^0 concentration) was recorded as a function of time.

As reported, the oxidative addition proceeds from the minor complex $SPd^0(PPh_3)_2$ (Scheme 3, eq 6).[8] Assuming that the equilibrium (5) ($K_1 = [SPd^0L_2][L]/[Pd^0L_3]$, L = PPh_3) is fast relative to the oxidative-addition step (6), the kinetic law for the overall reaction (7) is given in eq 8. Under stoichiometric conditions, at any time t, one

$$\frac{d[Pd^0]}{dt} = -\frac{kK_1[PhI][Pd^0]}{[L]} = -k_{app}[PhI][Pd^0] \quad (8)$$

has $[Pd^0] = xC_0$ (C_0 = initial concentration of $Pd^0(PPh_3)_4$ and $[PhI] = xC_0$. The integration of eq 8 gives eq 9.

$$\frac{1}{x} = \frac{kK_1C_0t}{[L]} + 1 = k_{app}C_0t + 1 \quad (9)$$

In agreement with the rate law in eq 9, the plot of $i_0/i = [Pd^0]_0/[Pd^0] = 1/x$ versus time was linear (Figure 1a, upper dashed line) (i = intensity of the oxidation current of $Pd^0(PPh_3)_3$ at t, i_0 = initial intensity of the oxidation current of $Pd^0(PPh_3)_3$). The straight-line intercept was unity, which is also in agreement with eq 9. The value of k_{app}, the apparent rate constant of the overall reaction (7), was then determined from the slope of the regression line (eq 9):[9] $k_{app} = 24\ M^{-1}\ s^{-1}$ (DMF, 25 °C).

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(9) However, in the absence of an excess of PPh_3, the concentration of PPh_3 (i.e., [L] in eqs 8 and 9) varies during the course of the oxidative addition due to its continuous release in the fast equation (5). Consequently, the variation of L concentration must be considered in the kinetic law (8) with $[L] = (2 - x)C_0$. The integration of eq 8 gives the new equation (9′): $1/x + 0.5 \ln x = 0.5kK_1t + 1$. The plot of $i_0/i + 0.5 \ln(i/i_0)$ versus time was linear (Figure 1c) (i = intensity of the oxidation current of $Pd^0(PPh_3)_3$ at t, i_0 = initial intensity of the oxidation current). The value of kK_1 was determined from the slope of the regression line (Figure 1c, eq 9′). $kK_1 = 0.062\ s^{-1}$. Since $k_{app} = kK_1/[L] = 24\ M^{-1}\ s^{-1}$ was obtained by application of the approximated eq 9 (see text), it ensues that eq 9 is a good approximation for [L] = 2.6 mM. This latter value is not far from the average value of 3 mM for PPh_3 concentration, which varies from the initial concentration of 2 mM to 4 mM at 100% conversion. Consequently, the simplified kinetic law in eq 9 can be used with a value of 2.6 mM for the average concentration of PPh_3. Since this simplifies greatly the presentation of the kinetics analysis given here, without introducing any significant bias in the kinetic treatment of the experimental data (see above), this simplification was used everywhere in the presentation of this paper.

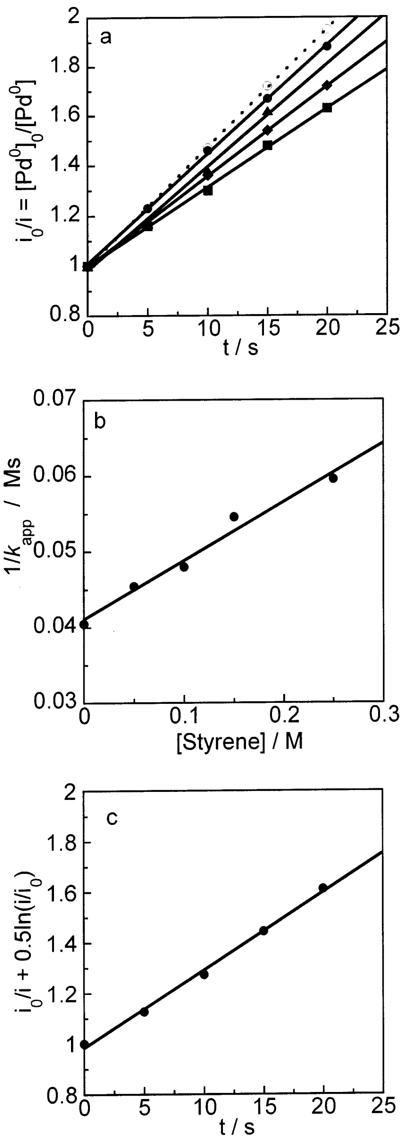
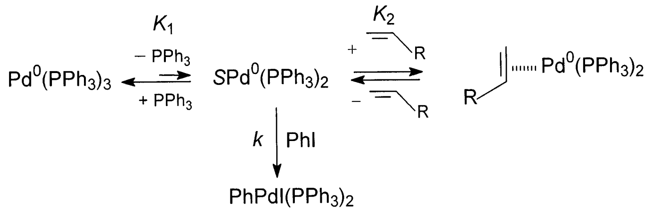
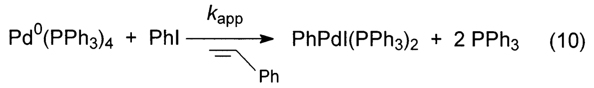


Figure 1. Oxidative addition of PhI (2 mM) to $Pd^0(PPh_3)_4$ (2 mM) in DMF (containing n-Bu_4NBF_4 0.3 M) at 25 °C, monitored by amperometry at a rotating-gold-disk electrode (diameter 2 mm, $\omega = 105$ rad s^{-1}) polarized at +0.2 V vs SCE in the absence or presence of styrene. (a) Plot of $i_0/i = [Pd^0]_0/[Pd^0] = 1/x$ versus time (i = intensity of the oxidation current of $Pd^0(PPh_3)_3$ at t, i_0 = initial intensity of the oxidation current of $Pd^0(PPh_3)_3$): $1/x = k_{app}C_0t + 1$ (eq 9 or 12). Oxidative addition was performed in the absence of styrene (○, dashed line) and in the presence of styrene at concentrations (M) of (●) 0.005, (▲) 0.1, (◆) 0.15, and (■) 0.3. (b) Plot of $1/k_{app}$ versus the styrene concentration (eq 12). (c) Plot of $i_0/i + 0.5\ln(i/i_0)$ versus time (eq 9′ in ref 9, $i_0/i = [Pd^0]_0/[Pd^0]$) in the absence of styrene (see Figure 1a caption for the definition of i and i_0).

Scheme 4. Mechanism of the Oxidative Addition of PhI to $Pd^0(PPh_3)_4$ in the Presence of an Alkene (R = Ph, CO_2Me)





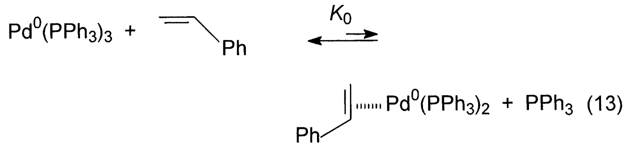
$$Pd^0(PPh_3)_4 + PhI \xrightarrow[\text{styrene}]{k_{app}} PhPdI(PPh_3)_2 + 2\,PPh_3 \quad (10)$$

In the presence of increasing amounts of styrene, the overall oxidative addition was found to be slower and slower, as evidenced by the decrease in the slopes of the plots of $i_0/i = [Pd^0]_0/[Pd^0] = 1/x$ versus time, determined for different styrene concentrations (Figure 1a). This suggests that the concentration of the active low ligated $Pd^0(PPh_3)_2$ moiety was decreased due to its increasing coordination by the alkene. Consequently, a new mechanistic scheme was considered with the overall reaction (10) (Scheme 4; R = Ph, $K_2 = [//{-}Pd^0L_2]/[Pd^0L_2][//]$, where the symbol // stands for the alkene). When any reaction between PhI and $(\eta^2\text{-}CH_2{=}CH{-}Ph)Pd^0(PPh_3)_2$ is neglected, the kinetic law becomes as expressed in eq 11. Under stoichiometric conditions, its integration

$$\frac{d[Pd^0]}{dt} = -\frac{kK_1[PhI][Pd^0]}{[L] + K_1K_2[//]} \qquad (11)$$

$$\frac{1}{x} = \frac{kK_1C_0t}{[L] + K_1K_2[//]} + 1 = k_{app}C_0t + 1 \qquad (12)$$

gives eq 12,[10] now with $1/k_{app} = [L]/kK_1 + K_2[//]/k$. Note that in the absence of styrene, $K_2[//]/k = 0$, so that one obtains eq 9. The plot of $1/k_{app}$ versus the styrene concentration (viz. constant [L][10]) was linear (Figure 1b), as predicted by the mechanism of Scheme 4: $1/k_{app} = a + b[//]$. The value $b = K_2/k = 0.077$ s was obtained from the slope, and that of $a = [L]/kK_1 = 0.041$ M s was calculated from the intercept. Using [L] = 2.6 mM,[10] one obtains $kK_1 = 0.063$ s^{-1}, which is identical with that determined in the absence of styrene ($kK_1 = 0.062$ s^{-1}).[9] The product of those two values allows the calculation of $K_0 = K_1K_2 = 4.8 \times 10^{-3}$, which is the value of the equilibrium constant K_0 of the overall equilibrium (13) ($K_0 = [//{-}Pd^0L_2][L]/[Pd^0L_3][//]$), in which a phosphine ligand is substituted from $Pd^0(PPh_3)_3$ by the styrene to form the new unreactive 16-electron complex $(\eta^2\text{-}CH_2{=}CHPh)Pd^0(PPh_3)_2$. Under comparable PPh_3 and styrene concentrations, eq 13 would play a negligible role, since it lies in favor of $Pd^0(PPh_3)_3$; however, it is worth noting that the effect would be reverse for higher styrene concentrations, as occurs in catalytic reactions.



$K_0 = 4.8{\times}10^{-3}$ (DMF, 25 °C)

Oxidative Addition of PhI to $Pd^0(PPh_3)_4$ in the Presence of Methyl Acrylate, in DMF. When a very electron deficient alkene such as methyl acrylate was considered, it was observed that the oxidation wave of

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[10] Due to the complexity of the kinetics laws in the presence of styrene, we use eq 11 but we consider a constant value of [L] in its integration (see note in ref 9). In eq 12, the value of [L] is thus considered as constant and equal to its average value of 2.6 mM over the reaction (see note in ref 9).

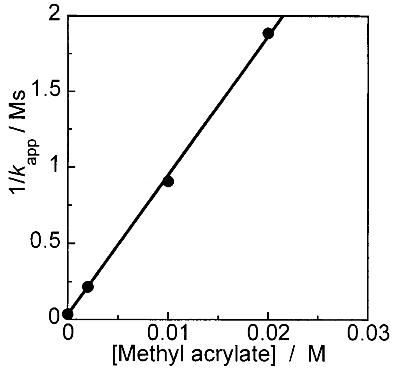
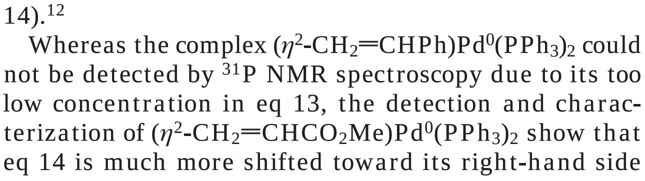


Figure 2. Oxidative addition of PhI (2 mM) to $Pd^0(PPh_3)_4$ (2 mM) in DMF (containing n-Bu_4NBF_4 0.3 M) at 25 °C, monitored by amperometry at a rotating-gold-disk electrode (diameter 2 mm, $\omega = 105$ rad s^{-1}) polarized at +0.3 V vs SCE in the presence of methyl acrylate. Plot of $1/k_{app}$ versus the methyl acrylate concentration (eq 12).

$Pd^0(PPh_3)_3$ (+0.14 V vs SCE) partially disappeared upon addition of methyl acrylate and a new oxidation peak appeared at a more positive potential (+0.48 V vs SCE). The oxidation peak current of this second peak increased at the expense of that of $Pd^0(PPh_3)_3$ upon increasing the methyl acrylate concentration. Investigation of a solution of $Pd^0(PPh_3)_4$ (8 mM) and methyl acrylate (0.8 M) in DMF by ^{31}P NMR spectroscopy showed a broad signal characteristic of $Pd^0(PPh_3)_3$ at −5.13 ppm and two thin doublets of similar integration (22.27 ppm, $J_{P-P} = 32$ Hz; 31.48 ppm, $J_{P-P} = 32$ Hz) characteristic of two chemically different PPh_3 groups ligated to one Pd atom, as expected for (η^2-$CH_2{=}CHCO_2Me$)$Pd^0(PPh_3)_2$ (eq 14).[11] Consequently, the addition of methyl acrylate to $Pd^0(PPh_3)_4$ results in the formation of a new Pd^0 complex ligated by the methyl acrylate (eq 14).[12]



$K_0 = 7.5$ (DMF, 25 °C)

Whereas the complex (η^2-$CH_2{=}CHPh$)$Pd^0(PPh_3)_2$ could not be detected by ^{31}P NMR spectroscopy due to its too low concentration in eq 13, the detection and characterization of (η^2-$CH_2{=}CHCO_2Me$)$Pd^0(PPh_3)_2$ show that eq 14 is much more shifted toward its right-hand side than eq 13. Consequently, for identical concentrations of styrene and methyl acrylate a higher decelerating effect is expected for the oxidative addition performed in the presence of methyl acrylate. In agreement with this expectation, the oxidative addition was considerably slowed when performed in the presence of methyl acrylate. The plot of $1/k_{app}$ versus the methyl acrylate concentration was linear (Figure 2), in agreement with the formulation in eq 12 and Scheme 4 (R = CO_2Me): $K_2/k = 92$ s for methyl acrylate versus 0.077 s for styrene (vide supra). Consequently, the value of the equilibrium constant K_2 is then 1200-fold higher for methyl acrylate than for styrene. This is consistent with the fact that the electron-deficient methyl acrylate is a much better ligand for the electron-rich $Pd^0(PPh_3)_2$ complex than styrene. The value of the equilibrium constant of eq 14 was calculated as above: $K_0 = 7.5$ (DMF, 25 °C). For identical concentrations of styrene and methyl acrylate, eq 14 is then considerably more shifted toward (η^2-$CH_2{=}CHCO_2Me$)$Pd^0(PPh_3)_2$ than is the equilibrium (13) toward (η^2-$CH_2{=}CHPh$)$Pd^0(PPh_3)_2$.

Scheme 5. Mechanism of the Oxidative Addition of PhI to the Pd⁰ Complex Generated from Pd(OAc)₂ + *n* Equiv of PPh₃ (*n* ≥ 4)

$$Pd^0(PPh_3)_3(OAc)^- \overset{K'_1}{\rightleftharpoons} Pd^0(PPh_3)_2(OAc)^- + PPh_3 \qquad (16)$$

$$Pd^0(PPh_3)_2(OAc)^- + PhI \xrightarrow{k'} PhPd(OAc)(PPh_3)_2 + I^- \qquad (17)$$

Overall reaction:

$$Pd^0(PPh_3)_3(OAc)^- + PhI \xrightarrow{k'_{app}} PhPd(OAc)(PPh_3)_2 + I^- + PPh_3 \qquad (18)$$

Oxidative Addition of PhI to $Pd^0(PPh_3)_3(OAc)^-$ (Generated from $Pd(OAc)_2$ and 5 Equiv of PPh_3) in the Presence of Styrene, in DMF. The catalytic precursor $Pd(OAc)_2$ associated with PPh_3 has been selected because it is commonly used in Heck reactions (eq 3).[2] We previously established that the addition of excess PPh_3 to $Pd(OAc)_2$ in DMF, leads to the formation of an anionic Pd^0 complex via the intramolecular reduction of $Pd(OAc)_2(PPh_3)_2$ by PPh_3, which is oxidized to the phosphine oxide (eq 15).[7] The oxidative addition of PhI proceeds as in Scheme 5: i.e., exclusively from the complex $Pd^0(PPh_3)_2(OAc)^-$,[7c] which represents a very minor fraction of the overall Pd^0 ($K'_1 = [Pd^0L_2(OAc)^-] \times [L]/[Pd^0L_3(OAc)^-]$; L = PPh_3).

$$Pd(OAc)_2 + 4PPh_3 + H_2O \rightarrow Pd^0(PPh_3)_3(OAc)^- + H^+ + AcOH + (O)PPh_3 \qquad (15)$$

To allow a meaningful comparison with the case of $Pd^0(PPh_3)_4$ investigated above (where the major complex is Pd^0L_3 and 1 equiv of free L is present initially in solution), the kinetics of the oxidative addition of PhI (2 mM) was determined in DMF at 25 °C from the anionic Pd^0 complex generated from $Pd(OAc)_2$ (2 mM) and 5 equiv of PPh_3 (major complex $Pd^0L_3(OAc)^-$, 1 equiv of free L, one L being oxidized (eq 15)). The oxidative addition was performed in the presence of 3 equiv of NEt_3, to neutralize the protons generated together with the Pd^0 complex (eq 15), which may react with the anionic $Pd^0(PPh_3)_2(OAc)^-$ to generate $Pd^0(PPh_3)_2$.[2d] Under stoichiometric conditions (1 equiv of PhI relative to $Pd^0(PPh_3)_2(OAc)^-$), the kinetic law was the same as that used for $Pd^0(PPh_3)_4$ (eq 9) and the rate constant of the overall reaction (18) was then determined: $k'_{app} = 22$ M^{-1} s^{-1} with $k'K'_1 = k'_{app}[L] = 0.057$ s^{-1}.[9] The value of $k' = 65$ M^{-1} s^{-1} was determined independently by reacting PhI and $Pd^0(PPh_3)_2(OAc)^-$, generated from $Pd(OAc)_2$ and 3 equiv of PPh_3.[7c] Consequently, the value of K'_1 was determined: $K'_1 = 9 \times 10^{-4}$ M. The value of $k'K'_1 = 0.057$ s^{-1} (Scheme 5) is very similar to that found for of $Pd^0(PPh_3)_4$ ($kK_1 = 0.062$ s^{-1}, Scheme 3). However, the values of k and K_1 remain unknown for $Pd^0(PPh_3)_4$. This unfortunately precludes any comparison of the equilibrium constants and rate

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[11] This complexation is very reminiscent of that of $Pd^0(PPh_3)_2$ by dba to form unreactive (η^2-dba)$Pd^0(PPh_3)_2$, which has been characterized by its oxidation peak and by two ^{31}P NMR signals.[8b]

[12] For Pd^0 complexes ligated by methyl acrylate, see also ref 5.

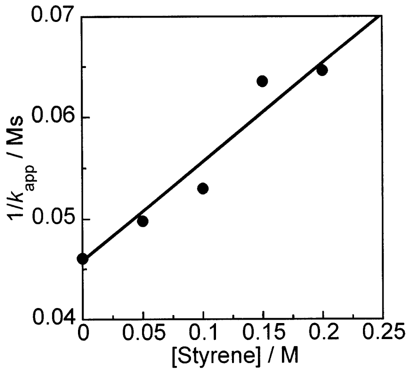
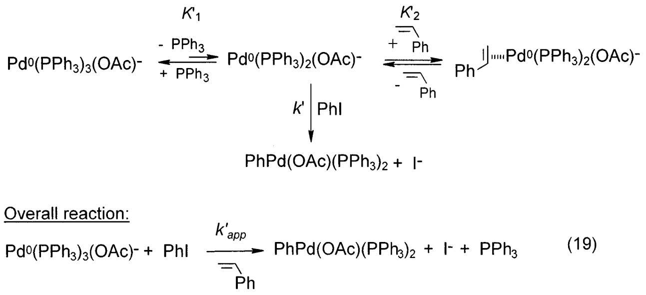


Figure 3. Oxidative addition of PhI (2 mM) to the $Pd^0(PPh_3)_3(OAc)^-$ generated from $Pd(OAc)_2$ (2 mM) and PPh_3 (10 mM) in DMF (containing 0.3 M n-Bu_4NBF_4) at 25 °C, monitored by amperometry at a rotating-gold-disk electrode (diameter 2 mm, $\omega = 105$ rad s^{-1}) polarized at +0.2 V vs SCE. The oxidative addition was performed in the absence or in the presence of styrene. Plot of $1/k'_{app}$ versus the styrene concentration (eq 20).

Scheme 6. Mechanism of the Oxidative Addition of PhI to $Pd^0(PPh_3)_3(OAc)^-$ in the Presence of Styrene

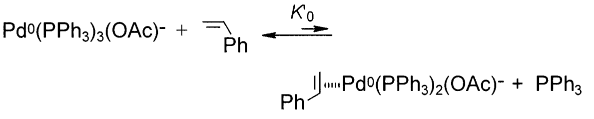


constants of the intrinsic oxidative additions of $Pd^0(PPh_3)_2$ and $Pd^0(PPh_3)_2(OAc)^-$.

In the presence of styrene, the oxidative addition was slower. We previously established that the complex $PhPd(OAc)(PPh_3)_2$, formed in the oxidative addition (eq 18), reacts with styrene to form stilbene and the Pd^0 catalyst, but this reaction is considerably slower than the oxidative addition.[7c] Nevertheless, it has been checked that no stilbene was formed (eq 3) over the time scale of the overall oxidative addition (20 min). Stilbene production required more longer times (hours)[7c] as well as the recycling of the Pd^0 catalyst. Consequently the investigated oxidative addition was not perturbed by any fortuitous recycling of the Pd^0 catalyst. Since styrene was present at the very first time of the oxidative addition, its coordination to the active Pd^0 complex occurs concurrently with the oxidative addition, as established above for $Pd^0(PPh_3)_4$, to form the unreactive 18-electron complex $(\eta^2\text{-}CH_2{=}CHPh)Pd^0(PPh_3)_2(OAc)^-$ (Scheme 6, $K'_2 = [//\text{-}Pd^0L_2(OAc)^-]/[Pd^0L_2(OAc)^-][//]$). The kinetic law (20) is then identical with eq 12

$$1/k'_{app} = [L]/k'K'_1 + K'_2[//]/k' \qquad (20)$$

except for the exact meaning of the individual rate constants (Scheme 6). The plot of $1/k'_{app}$ versus the styrene concentration was linear (Figure 3), thus establishing the validity of Scheme 6 and eq 20: $1/k'_{app} = a + b[//]$. The value of $K'_2/k' = 0.097$ s was determined from the slope and $k'K'_1 = 0.057$ s^{-1} from the intercept. This latter value agrees completely with that found in the absence of styrene (vide supra). The product of those two values affords $K'_0 = K'_1K'_2 = 5.5 \times 10^{-3}$, which is the equilibrium constant of the overall eq 21, in which



(21)

$K'_0 = 5.5 \times 10^{-3}$ (DMF, 25 °C)

one phosphine ligand is substituted from $Pd^0(PPh_3)_3(OAc)^-$ by the styrene to form the new unreactive 18-electron complex $(\eta^2\text{-}CH_2{=}CH{-}Ph)Pd^0(PPh_3)_2(OAc)^-$. Since $K'_1 = 9 \times 10^{-4}$ M, then $K'_2 = 61$ M^{-1} (Scheme 6). The value of K'_0 is rather low, which means that the substitution in eq 21 is not favorable for comparable concentrations of PPh_3 and styrene. However, in catalytic Heck reactions where the styrene concentration might be, for example, 100 times higher than that of the catalytic Pd^0, the concentration of $(\eta^2\text{-}CH_2{=}CHPh)Pd^0(PPh_3)_2(OAc)^-$ would be half of that of $Pd^0(PPh_3)_3(OAc)^-$ and the rate of the overall oxidative addition would thus be divided by 1.4. The decelerating effect will be more important in the absence of any free PPh_3: i.e., when $Pd^0(PPh_3)_2(OAc)^-$ is generated quantitatively from $Pd(OAc)_2$ and 3 equiv of PPh_3.[7c] Indeed, in the absence of any free PPh_3, only the right part of Scheme 6 must be considered with the equilibrium constant K'_2 and $k'_{app} = k'/(1 + K'_2[//])$. From the value of K'_2 determined above, one predicts that, for a styrene concentration 100 times higher than that of the catalytic Pd^0, the rate of the oxidative addition would be divided by ca. 13.

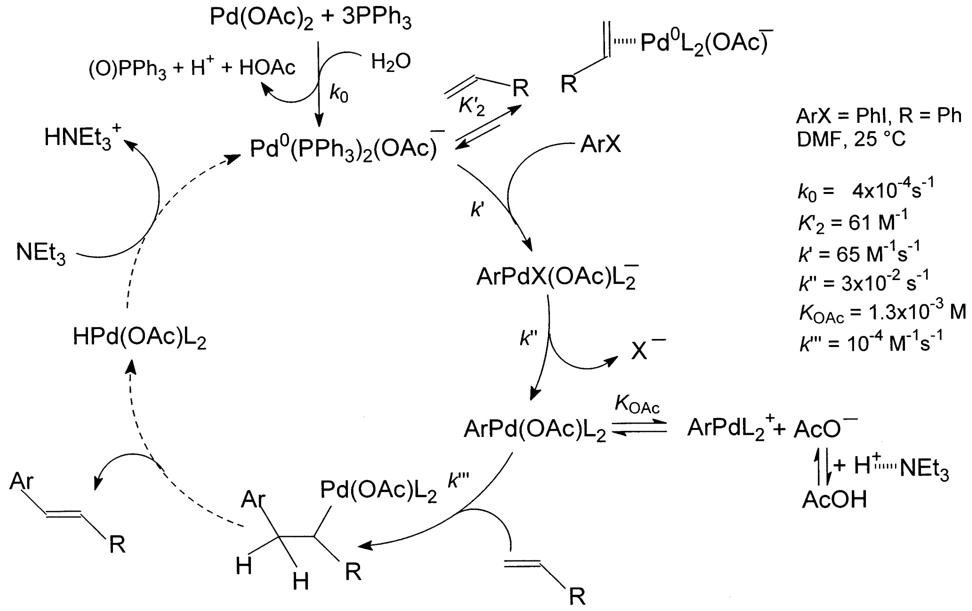
Consequently, the mechanistic scheme of the Heck reaction, when catalyzed by $Pd(OAc)_2$ associated with 3 equiv of PPh_3, established in previous works[2d] must be improved by the introduction of the alkene at the level of the oxidative addition (Scheme 7), including the value of K_2' determined in the present work (the values of k_0,[7b] k',[7c] k'',[7c] k''',[7c] and K_{OAc}[7d] have been determined in previous works).

Conclusion

In DMF, the oxidative addition of PhI to $Pd^0(PPh_3)_4$ or to the anionic $Pd^0(PPh_3)_3(OAc)^-$ (generated from $Pd(OAc)_2$ and 5 equiv of PPh_3) is slower in the presence of an alkene such as styrene or methyl acrylate. The concentration of the reactive Pd^0 complex decreases due to its coordination to the alkene to form the unreactive complexes: $(\eta^2\text{-}CH_2{=}CHPh)Pd^0(PPh_3)_2$, $(\eta^2\text{-}CH_2{=}CHCO_2Me)Pd^0(PPh_3)_2$, or $(\eta^2\text{-}CH_2{=}CHPh)Pd^0(PPh_3)_2(OAc)^-$, accordingly.

Consequently, a more elaborate mechanistic scheme is proposed for the Heck reaction, when catalyzed by $Pd(OAc)_2$ associated with 3 equiv of PPh_3 (Scheme 7), in which the alkene plays a role in the oxidative addition, by stocking part of the active Pd^0 under the unreactive complex $(\eta^2\text{-}CH_2{=}CHR)Pd^0(PPh_3)_2(OAc)^-$. The oxidative addition is usually a fast reaction (especially with aryl iodides). It is noteworthy that the nucleophile interference by slowing down the oxidative addition is then in favor of a higher efficiency for the catalytic cycle, by bringing the rate of the oxidative addition closer to that of the carbopalladation, i.e., the

Scheme 7. Mechanism of the Heck Reaction Catalyzed by $Pd(OAc)_2$ Associated with 3 Equiv of PPh_3



nucleophilic attack on the aryl−Pd^{II} complexes formed in the oxidative addition, which is usually rate determining.[13,14]

Experimental Section

^{31}P NMR spectra were recorded in DMF containing 10% CD_3COCD_3, on a Bruker spectrometer (101 MHz) using H_3PO_4 as an external reference. Voltammetry at a rotating-disk electrode was performed with a homemade potentiostat and a Radiometer Analytical GSTP4 waveform generator and recorded on a Nicolet 301 oscilloscope.

DMF was distilled from calcium hydride under vacuum and kept under argon. Phenyl iodide, styrene, methyl acrylate, and triethylamine were obtained commercially (Acros) and used after filtration on alumina. $Pd(OAc)_2$ and PPh_3 were obtained commercially (Acros) and used without purification. $Pd^0(PPh_3)_4$ was prepared according to a described procedure.[15] $Pd^0(PPh_3)_3(OAc)^-$ was synthesized from $Pd(OAc)_2$ and 5 equiv of PPh_3 in the presence of NEt_3 (3 equiv).[7c]

Electrochemical Setup and Electrochemical Procedure for Kinetic Measurements. Experiments were carried out in a three-electrode cell connected to a Schlenk line. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Radiometer Analytical) separated from the solution by a bridge filled with 3 mL of DMF containing n-Bu_4NBF_4 (0.3 M). A 15 mL portion of DMF containing n-Bu_4NBF_4 (0.3 M) was poured into the cell followed by $Pd^0(PPh_3)_4$ (34 mg, 0.03 mmol). The kinetics of the oxidative addition of PhI (6.12 mg, 0.03 mmol) was monitored at a rotating gold-disk electrode (i.d. 2 mm, inserted into a Teflon holder, Radiometer Analytical EDI 65109) polarized at +0.2 V, with an angular velocity of 105 rad s^{-1} (Radiometer Analytical Controvit) in the presence of an alkene added before PhI (styrene in the range 0−0.3 M or methyl acrylate in the range 0−0.02 M).

The same procedure was adopted for the investigation of the reactivity of PhI with $Pd^0(PPh_3)_2(OAc)^-$ in the presence of styrene (in the range 0−0.2 M).

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(13) Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254.

(14) The base NEt_3, used in Heck reactions, also plays a similar role. The oxidative addition is slower in the presence of NEt_3 and the carbopalladation faster.[2d]

(15) Rosevear, D. T.; Stone, F. G. *J. Chem. Soc. A* **1968**, 164.