Decelerating Effect of Alkynes in the Oxidative Addition of Phenyl Iodide to Palladium(0) Complexes in Palladium-Catalyzed Multicomponent Reactions and Sonogashira Reactions

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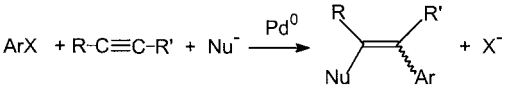
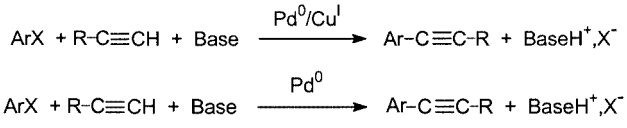
The oxidative addition of PhI to $[Pd^0(PPh_3)_4]$ in DMF is slower when performed in the presence of the terminal alkynes (PhC≡CH, EtO_2C–C≡CH) that are reagents in palladium-catalyzed Sonogashira or multicomponent reactions. The concentration of the reactive $[Pd^0(PPh_3)_2]$ complex decreases because of its partial coordination to the alkyne to form $[(\eta^2\text{-}RC{\equiv}CH)Pd^0(PPh_3)_2]$ (R = Ph, $EtCO_2$), which is in equilibrium with $[Pd^0(PPh_3)_2]$. The complex $[(\eta^2\text{-}PhC{\equiv}CH)Pd^0(PPh_3)_2]$ was found to be unreactive whereas $[(\eta^2\text{-}EtO_2C\text{–}C{\equiv}CH)Pd^0(PPh_3)_2]$ was found to be the unique reactive complex at high concentrations of EtO_2C–C≡CH. As has been reported for alkenes, terminal alkynes play an unexpected role because they interfere in the oxidative addition before their usual reactions in the carbopalladation and transmetallation steps that follow it. Decreasing the rate of the fast oxidative addition with PhI may promote the efficiency of the catalytic cycle by bringing its rate closer to that of the slower carbopalladation or transmetallation steps.

Introduction

Alkynes may be activated through palladium-catalyzed reactions such as three-component reactions (Scheme 1)[1–3] or Sonogashira reactions (terminal alkynes; Scheme 2).[4,5]

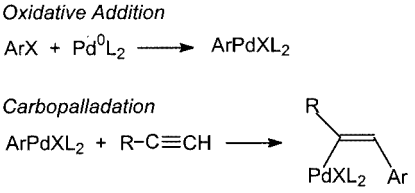


Scheme 1



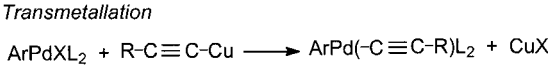
Scheme 2

In multicomponent reactions (Scheme 1),[1–3] the alkynes react in the second step of the catalytic cycle (*carbopalladation* step), i.e., with the arylpalladium(II) complex that was generated in the *oxidative addition* of the aryl halide to a palladium(0) complex (Scheme 3).



Scheme 3

The mechanism of the Sonogashira reactions has not yet been established clearly. In the process using a copper co-catalyst, the reaction is considered to be a cross-coupling reaction.[4] Again, the alkynes are believed to be involved in the second step of the catalytic cycle, i.e., in a *transmetallation* step with the arylpalladium(II) complex via an alkynylcopper intermediate generated in situ (Scheme 4).



Scheme 4

In the copper-free process,[5] even if the origin of the alkynilide remains problematic, it is also believed to be involved in the second step of the catalytic cycle (*transmetallation*).

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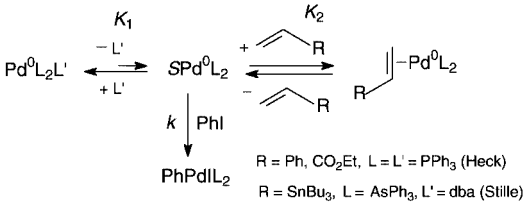
It has been established that in Heck reactions performed with alkenes (styrene, methyl acrylate)[6,7] or in Stille reactions performed with a vinyltin derivative (CH_2=CH−$SnBu_3$),[8] the nucleophiles play a role before the *carbopalladation* (Heck reaction) or *transmetallation* (Stille reaction) steps, by having a decelerating effect on the oxidative addition. Indeed, the oxidative addition is slower in the presence of the nucleophile, because of a partial coordination of the active Pd^0 complex by the C=C bond of the nucleophile, which results into unreactive Pd^0 complexes (Scheme 5)[7,8] or very weakly reactive Pd^0 complexes.[6]



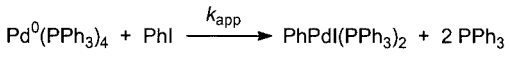
Scheme 5. Mechanism of the oxidative addition of PhI to [Pd^0] complexes in the presence of alkenes or vinyl(tributyl)tin in DMF

Consequently, we were interested in investigating the role of alkynes involved in palladium-catalyzed multicomponent (Scheme 1) or Sonogashira (Scheme 2) reactions toward the kinetics of the oxidative additions, because they possess a C≡C bond that is able to coordinate to Pd^0 complexes. We report herein our investigations that generalize the role played by unsaturated nucleophiles in the kinetics of oxidative additions, i.e., before their implication in the classical carbopalladation or transmetallation steps.

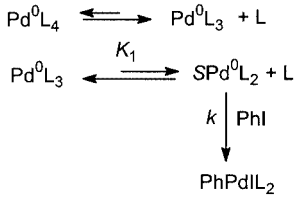
Results and Discussion

Oxidative Addition of PhI to [$Pd^0(PPh_3)_4$] in DMF in the Presence of Phenylacetylene

The mechanism of the oxidative addition of PhI to [$Pd^0(PPh_3)_4$] (Scheme 6) is reported in Scheme 7.[9,10]



Scheme 6



Scheme 7. Mechanism of the oxidative addition of PhI to [$Pd^0(PPh_3)_4$] (S = solvent, L = PPh_3)

The corresponding kinetic law is given by Equation (1), where $k_{app} = kK_1/[L]$

$$\frac{d[Pd^0]}{dt} = -\frac{kK_1[PhI][Pd^0]}{[L]} = -k_{app}[PhI][Pd^0] \quad \text{with } k_{app} = kK_1/[L] \tag{1}$$

Under stoichiometric conditions, when [PhI] = [$Pd^0(PPh_3)_4]_0 = c_0$, the integration of Equation (1) gives Equation (2), where $x = [Pd^0]_t/[Pd^0]_0$.[11]

$$\frac{1}{x} = k_{app}C_0t + 1 \tag{2}$$

As reported, the kinetics of the oxidative addition of PhI to [$Pd^0(PPh_3)_4$] in DMF (containing $n$$Bu_4NBF_4$, 0.3 M) can be monitored by amperometry performed at a rotating disk electrode, polarized at +0.2 V vs. SCE, i.e., on the oxidation wave of [$Pd^0(PPh_3)_3$][9,10] The decay of the oxidation current (proportional to the Pd^0 concentration) was recorded versus time. The value of k_{app}, the apparent rate constant of the overall oxidative addition (Scheme 6), was then determined from the slope of the regression line obtained by plotting $i_0/i = [Pd^0]_0/[Pd^0]_t = 1/x$ versus time [Equation (2), uppermost line in Figure 1]: $k_{app} = 24\ M^{-1}\ s^{-1}$ (c_0 = 2 mM). The value of kK_1 was also calculated: $kK_1 = 0.062\ s^{-1}$ (DMF, 25 °C).[11]

When PhC≡CH (200 equiv.) was added to a solution of [$Pd^0(PPh_3)_4$] (2 mM) in DMF (containing $n$$Bu_4NBF_4$, 0.3 mM), the partial decay of the oxidation peak of [$Pd^0(PPh_3)_3$] at E^p_{ox} = +0.08 V was observed together with a small shift toward more-positive potential (+0.10 V), which is indicative of a CE mechanism. No other oxidation peak was detected within the potential range investigated (up to +1 V). A ^{31}P NMR spectrum of a solution of [$Pd^0(PPh_3)_4$] (12 mM) and PhC≡CH (2.4 M) in DMF (containing 10% [D_6]acetone) exhibited, besides the broad signal of [$Pd^0(PPh_3)_3$] at δ = 0.61 ppm, two broad signals ($\Delta\nu_{1/2}$ = 20 Hz) of the same magnitude at δ = 25.44 and 28.4 ppm, which are characteristic of two magnetically nonequivalent phosphane units. A new complex was then formed by addition of PhC≡CH to [$Pd^0(PPh_3)_4$] in DMF. The formation of a Pd^{II} complex by activation of the C−H bond, such as [*trans*-PhC≡C−Pd$H(PPh_3)_2$],[12−14] is excluded because it would contain two magnetically equivalent phosphane units. Moreover, no signal that is characteristic of a hydride was detected by ^1H NMR spectroscopy in $CDCl_3$.[12−14] Consequently, the new complex generated by addition of PhC≡CH to [$Pd^0(PPh_3)_4$] must result from complexation of the C≡C bond, [(η^2-PhC≡CH)$Pd^0(PPh_3)_2$] (Scheme 8), as has been observed for alkenes (styrene, methyl acrylate).[7] [(η^2-PhC≡CH)$Pd^0(PPh_3)_2$] was characterized by FAB mass spectrometry (m/z = 733 $[M + H]^+$, 630 [M − PhC≡CH]).

The kinetics of the oxidative addition of PhI (c_0 = 2 mM) to [$Pd^0(PPh_3)_4$] (c_0 = 2 mM) in DMF in the presence of

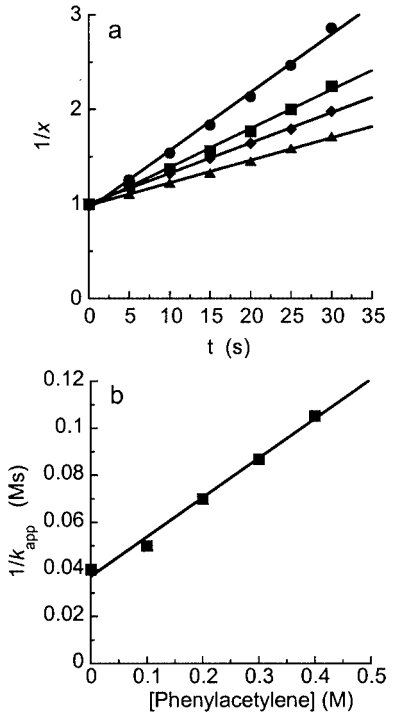
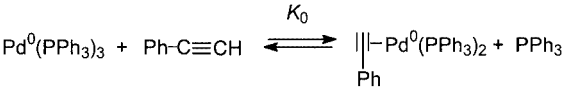
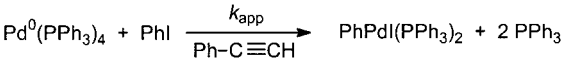


Figure 1. Oxidative addition of PhI (2 mM) to $[Pd^0(PPh_3)_4]$ (2 mM) in DMF (containing nBu_4NBF_4 0.3 M), in the absence or presence of phenylacetylene, as monitored by amperometry at a rotating gold disk electrode (diameter: 2 mm; $\omega = 105$ rad s^{-1}) polarized at +0.2 V vs. SCE, at 25 °C. (a) Plot of $1/x = i_0/i = [Pd^0]_0/[Pd^0]_t$ vs. time (i = intensity of the oxidation current of $[Pd^0(PPh_3)_3]$ at t; i_0 = initial intensity of the oxidation current of $[Pd^0(PPh_3)_3]$: $1/x = k_{app}c_0t + 1$ [Equation (2)]). Oxidative addition performed in the absence of phenylacetylene (filled circles) and in the presence of phenylacetylene: (filled rectangle) 0.1; (filled trapezoid) 0.2; (filled triangle) 0.4 M. (b) Plot of $1/k_{app}$ vs. concentration of phenylacetylene [Equation (5)]. The value of k_{app} was determined from the slope of the regression lines obtained in Figure 1, a



Scheme 8

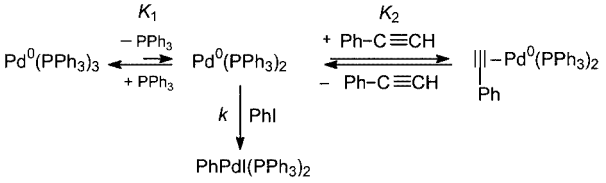
various amounts of PhC≡CH (0.1−0.4 M) were investigated by amperometry (Scheme 9), as performed above in the absence of PhC≡CH. PhC≡CH was added to $[Pd^0(PPh_3)_4]$ before the introduction of PhI.



Scheme 9

The overall oxidative addition was slowed down in the presence of increasing amounts of phenylacetylene, as evidenced by the decay of the slopes of the plots of $1/x$ versus time at the different PhC≡CH concentrations (Figure 1, a).

This behavior is similar to that already observed to occur in the presence of alkenes (styrene, methyl acrylate).[7] The occurrence of this process implies that the concentration of the active $Pd^0(PPh_3)_2$ species decreases because of its reversible coordination by the alkyne, which generates the unreactive complex, $[(\eta^2\text{-PhC}\equiv\text{CH})Pd^0(PPh_3)_2]$, according to the mechanism presented in Scheme 10.



Scheme 10. Mechanism of the oxidative addition of PhI to $[Pd^0(PPh_3)_4]$ in DMF in the presence of phenylacetylene

For PhI and $[Pd^0(PPh_3)_4]$ under stoichiometric conditions, a new kinetic law is expressed as in Equation (3) and (4).[15]

$$\frac{d[Pd^0]}{dt} = -\frac{kK_1[PhI][Pd^0]}{[L] + K_1K_2[alkyne]} \quad (3)$$

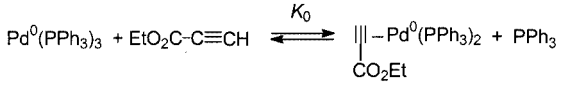
$$\frac{1}{x} = \frac{kK_1C_0t}{[L] + K_1K_2[alkyne]} + 1 = k_{app}C_0t + 1 \quad (4)$$

$$\frac{1}{k_{app}} = \frac{[L]}{kK_1} + \frac{K_2[alkyne]}{k} \quad (5)$$

The plot of $1/k_{app}$ against the PhC≡CH concentration is linear (Figure 1, b) — $1/k_{app} = 0.0369 + 0.167$[alkyne] — which is in agreement with the mechanism of Scheme 10 and Equation (5). The value of $[L]/kK_1 = 0.0369$ Ms was obtained from the intercept and that of $K_2/k = 0.167$ s from the slope [Equation (5)]. Using [L] = 2.6 mM,[15] one obtains $kK_1 = 0.07$ s^{-1}. This value allows the calculation of the equilibrium constant K_0 for the overall equilibrium in Scheme 8 ($K_0 = [(\eta^2\text{-alkyne})Pd^0L_2][L]/[Pd^0L_3][alkyne]$): $K_0 = K_1K_2 = 0.012$ (DMF, 25 °C)

Oxidative Addition of PhI to $[Pd^0(PPh_3)_4]$ in DMF in the Presence of Ethylpropiolate, $EtO_2C-C\equiv C-H$

When two equiv. of $EtO_2C-C\equiv CH$ (34 mM) were added to a solution of $[Pd^0(PPh_3)_4]$ (17 mM) in [D_6]acetone, the ^1H NMR spectrum exhibited two broad singlets at $\delta = 4.21$ and 1.26 ppm instead of the triplet ($\delta = 1.28$ ppm, $J = 7$ Hz, 3 H) and quadruplet ($\delta = 4.23$ ppm, $J = 7$ Hz, 2 H), respectively that are characteristic of the CH_3-CH_2 protons in the free alkyne, $EtO_2C-C\equiv C-H$. Similarly, the thin singlet of the C−*H* proton of free $EtO_2C-C\equiv CH$ was no longer detected at $\delta = 3.76$ ppm, but, instead, a broad singlet appeared at $\delta = 2.86$ ppm. This feature establishes that $EtO_2C-C\equiv CH$ is involved in an equilibrium with the initial Pd^0 complex and results in average signals for the free and the coordinated $EtO_2C-C\equiv CH$ (Scheme 11).



Scheme 11

A ^{31}P NMR spectrum of $[Pd^0(PPh_3)_4]$ (16 mM) in DMF (containing 10% $[D_6]$acetone) exhibited, after addition of $EtO_2C-C\equiv CH$ (0.16 M), a broad signal ($\Delta\nu_{1/2}$ = 47 Hz) for $[Pd^0(PPh_3)_3]$ at $\delta = -5.17$ ppm, i.e., very close to that of free PPh_3 ($\delta = -5.25$ ppm, not detected here), which indicates that the amount of $[Pd^0(PPh_3)_3]$ in the equilibrium of Scheme 11 was very low. A second broad signal ($\Delta\nu_{1/2}$ = 78 Hz) was observed at δ = 30.8 ppm which we assign to $[(\eta^2\text{-}EtO_2C-C\equiv CH)Pd^0(PPh_3)_2]$ (Scheme 11). The equivalence of the two phosphane ligands in that complex may be due to a fast internal rotation of the alkyne ligand, which is in agreement with the broadening observed for the signals of the protons of the coordinated $EtO_2C-C\equiv CH$ unit in the ^1H NMR spectrum (vide supra). $[(\eta^2\text{-}EtO_2C-C\equiv CH)Pd^0(PPh_3)_2]$ was characterized by FAB mass spectrometry (m/z = 729 $[M + H]^+$, 630 $[M - EtCO_2C\equiv CH]$).

When 1 equiv. of $EtO_2C-C\equiv CH$ was added to a solution of $[Pd^0(PPh_3)_4]$ (2 mM) in DMF (containing nBu_4NBF_4, 0.3 M), the oxidation peak of $[Pd^0(PPh_3)_3]$ at +0.08 V was no longer observed, which excluded a priori the investigation of the kinetics of the oxidative addition by amperometry. This problem was circumvented by the addition of excess PPh_3 (10 equiv.), which shifted the equilibrium in Scheme 11 towards its left-hand side so that $[Pd^0(PPh_3)_3]$ could be detected by its oxidation peak and, consequently, the kinetics of the oxidative addition could be monitored as above by amperometry. The kinetics of the oxidative addition of PhI (c_0 = 2 mM) to $[Pd^0(PPh_3)_4]$ (c_0 = 2 mM) were then investigated in DMF in the presence of PPh_3 (20 mM) both in the absence and presence (5 to 30 mM) of $EtO_2C-C\equiv CH$ (Scheme 12).

$$Pd^0(PPh_3)_4 + PhI + 10\ PPh_3 \xrightarrow[EtO_2C-C\equiv CH]{k_{app}} PhPdI(PPh_3)_2 + 12\ PPh_3$$

Scheme 12

The oxidative addition became slower upon increasing the $EtO_2C-C\equiv CH$ concentration. A saturation effect was observed, however, at high $EtO_2C-C\equiv CH$ concentrations, as evidenced by the plot of $1/k_{app}$ vs. $[EtO_2C-C\equiv CH]$ (Figure 2). The value of $1/k_{app}$ varied linearly with $[EtO_2C-C\equiv CH]$ at low concentrations (< 0.012 M), as had been observed for $PhC\equiv CH$ (Figure 1, b), whereas it was constant at high concentrations (> 0.02 M) (Figure 2).

This behavior suggests that at low concentrations, $[Pd^0(PPh_3)_2]$ remained the major reactive species, but it was present at lower concentration because of its complexation to $EtO_2C-C\equiv CH$. At high concentrations of $EtO_2C-C\equiv CH$, when the $[Pd^0(PPh_3)_2]$ concentration became very low as a result of the formation of $[(\eta^2\text{-}EtO_2C-C\equiv CH)Pd^0(PPh_3)_2]$ (the equilibrium depicted in Scheme 11), this latter, weakly reactive species was, nevertheless, sufficiently reactive to take over the role of active catalyst. $[(\eta^2\text{-}EtO_2C-C\equiv CH)Pd^0(PPh_3)_2]$ became the major reactive complex, once the equilibrium depicted in Scheme 11 was totally shifted to its right-hand side (Scheme 13).

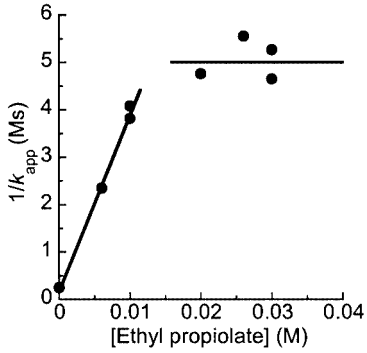
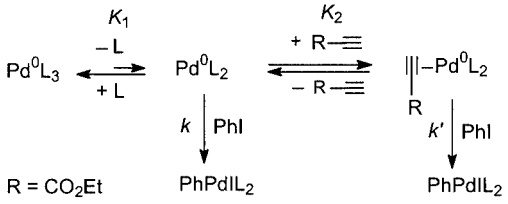


Figure 2. Oxidative addition of PhI (2 mM) to $[Pd^0(PPh_3)_4]$ (2 mM) in DMF (containing nBu_4NBF_4 0.3 M) in the presence of $EtO_2C-C\equiv CH$, monitored by amperometry at a rotating gold disk electrode (i.d. 2 mm, ω = 105 rad s^{-1}) polarized at +0.2 V vs. SCE, at 25 °C. Plot of $1/k_{app}$ vs. the concentration of ethyl propiolate



Scheme 13. Mechanism of the oxidative addition of PhI to $[Pd^0(PPh_3)_4]$ in DMF in the presence of ethyl propiolate (L = PPh_3)

According to Scheme 13, the kinetic law is given by Equation (6)–(8).[16]

$$\frac{d[Pd^0]}{dt} = -\frac{[PhI][Pd^0](k + k'K_2[alkyne])}{[L]/K_1 + K_2[alkyne]} \quad (6)$$

$$\frac{1}{x} = \frac{(k + k'K_2[alkyne])C_0t}{[L]/K_1 + K_2[alkyne]} + 1 = k_{app}C_0t + 1 \quad (7)$$

$$\frac{1}{k_{app}} = \frac{[L]/K_1 + K_2[alkyne]}{k + k'K_2[alkyne]} \quad (8)$$

At high concentrations of $EtO_2C\equiv C\text{-}H$ (> 0.02 M), K_2[alkyne] > [L]/K_1 and $k'K_2$[alkyne] > k. Thus, one obtains Equation (9), where k' = 0.2 $M^{-1}s^{-1}$ (DMF, 25 °C), as determined from Figure 2.

$$\frac{1}{k_{app}} = \frac{1}{k'} \quad (9)$$

At low concentrations of $EtO_2C\equiv C\text{-}H$ (< 0.012 M), $k'K_2$[alkyne] < k, so that one obtains Equation (10), which is similar to Equation (4) that was established above for $PhC\equiv CH$.

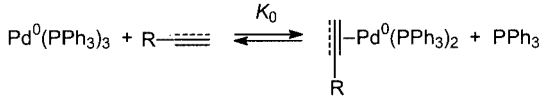
$$\frac{1}{k_{app}} = \frac{[L]}{kK_1} + \frac{K_2[alkyne]}{k} \quad (10)$$

The value of $[L]/kK_1 = 0.25$ Ms was obtained from the intercept with $kK_1 = 0.08\ s^{-1}$ (Figure 2). The value of $K_2/k = 360$ s was given by the slope [Equation (10)]. The product of those two values allows the equilibrium constant K_0 to be calculated for the overall equilibrium presented in Scheme 11: $K_0 = K_1K_2 = 29$ (DMF, 25 °C).

Table 1. Equilibrium constants K_0 for the reaction of $[Pd^0(PPh_3)_4]$ with alkenes[7] and alkynes in DMF at 25 °C (Scheme 14)

	PhCH=CH$_2$	PhC≡CH	MeO$_2$C−CH=CH$_2$	EtO$_2$C−C≡CH
K_0	0.0048	0.012	7.5	29

The values of K_0 determined here are collected in Table 1 and are compared to the values obtained with alkenes[7] (Scheme 14).



Scheme 14

As expected, alkynes are better ligands for $[Pd^0(PPh_3)_2]$ than are alkenes. Electron-deficient alkynes or alkenes are better ligands for the electron-rich $[Pd^0(PPh_3)_2]$. The comparative affinity of EtO$_2$C−C≡CH or PhC≡CH for $[Pd^0(PPh_3)_2]$ is given by their respective values of K_2, whose ratio is obtained from their respective values of K_0. Since K_1 is identical for both, the affinity of the electron-deficient EtO$_2$C−C≡CH for the electron-rich $[Pd^0(PPh_3)_2]$ (expressed by K_2) is, therefore, 2400-times higher than that of PhC≡CH.

The non-terminal alkynes PhC≡CMe and PhC≡CCO$_2$Et affect the rate of the oxidative addition of PhI to $[Pd^0(PPh_3)_4]$ in DMF at 25 °C by having a very low decelerating effect, even when added in large concentrations (0.3 M). This observation is indicative of a very low affinity of the more-electron-rich PhC≡CMe for $[Pd^0(PPh_3)_2]$.

Conclusions

In DMF, the oxidative addition of PhI to $[Pd^0(PPh_3)_4]$ is slower in the presence of the terminal alkynes (PhC≡CH, EtO$_2$C−C≡CH) that are reagents in the palladium-catalyzed Sonogashira or multicomponent reactions. The concentration of the reactive Pd^0 complex decreases as a result of its coordination to the alkyne to form the unreactive complex $[(\eta^2\text{-PhC≡CH})Pd^0(PPh_3)_2]$, whereas $[(\eta^2\text{-EtO}_2C-C≡CH)Pd^0(PPh_3)_2]$ was found to be reactive at high concentrations of EtO$_2$C−C≡CH. We do not exclude the possibility that $[(\eta^2\text{-PhC≡CH})Pd^0(PPh_3)_2]$ might be involved in the oxidative addition at very high concentrations of PhC≡CH (> 0.4 M). This process was not observed, however, under our experimental conditions, since it would require so large an amount of PhC≡CH that the medium properties might be affected simultaneously.

As has been reported for alkenes, terminal alkynes might play an unexpected role since they influence the rate of the oxidative addition before their implication in the carbopalladation or transmetallation steps. Decreasing the rate of the fast oxidative addition with aryl iodides may favor the efficiency of the catalytic cycle by bringing its rate closer to that of the slower carbopalladation or transmetallation steps.[17]

Experimental Section

Materials: ^{31}P NMR spectra were recorded in DMF containing 10% [D$_6$]acetone, using a Bruker spectrometer (101 MHz) having H_3PO_4 as an external reference. Voltammetry at a rotating disk electrode was performed with a home-made potentiostat and a waveform generator and were recorded on an oscilloscope.

DMF was distilled from calcium hydride under vacuum and kept under argon. Phenyl iodide, phenylacetylene and ethyl propiolate were commercial grade and were used after filtration through alumina. PPh_3 was commercial grade and used without purification. $[Pd^0(PPh_3)_4]$ was prepared according to a described procedure.[18]

Electrochemical Set-Up and Electrochemical Procedure for Kinetic Measurements: Experiments were carried out in a three-electrode thermostatted 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 separated from the solution by a bridge filled with DMF (3 mL) containing nBu$_4$NBF$_4$ (0.3 M). DMF (15 mL) containing nBu$_4$NBF$_4$ (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) polarized at +0.2 V, with an angular velocity of 105 rad·s^{-1} in the presence of an alkyne that was added prior to PhI. Phenylacetylene was present in the range 0.1−0.4 M and ethyl propiolate in the range 0.01−0.03 M.

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[11] In the absence of excess PPh_3, the variation of its concentration must be considered in the kinetic law [Equation (1)] whose integration gives Equation (2)′: $1/x + 0.5\ln x = 0.5kK_1t + 1$. The value of kK_1 was determined from the slope of the regression line obtained by plotting $1/x + 0.5\ln x$ against time: $kK_1 = 0.062\ s^{-1}$. Since $k_{app} = kK_1/[L] = 24\ M^{-1}\ s^{-1}$ was obtained by application of the approximate Equation (2) (see text), Equation (2) can be considered as a good approximation with an average value for [L] of 2.6 mM. This value is not far from the average value of 3 mM for the concentration of PPh_3, which varies from the initial concentration of 2 mM to 4 mM at 100% conversion. Consequently, the simplified kinetic law in Equation (2) can be used with a value of 2.6 mM for the average concentration of PPh_3 under our conditions.
[12] Such a complex was generated by reacting $[Pd^0(PPh_3)_4]$ with PhC≡CH at 80 °C, i.e., upon more drastic conditions than that investigated here. See the reported by: G. A. Chukhadzhyan, Z. K. Evoyan, L. N. Melkonyan, *J. Gen. Chem.* **1975**, *45*, 1096−1098. For reviews, see refs.[13,14].
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[15] Because of the complexity of the kinetic law in the presence of the alkyne, a constant value of [L] was considered for the integration of Equation (3) to be equal to its average value of 2.6 mM (see ref.[11]) for all reactions performed here (c_0 = 2 mM).
[16] In this case, [L] is constant because PPh_3 was added in excess before the introduction of $EtO_2C-C\equiv CH$ and PhI.
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