# Rate and Mechanism of the Oxidative Addition of Phenyl Iodide to $Pd^0$ Ligated by Triphenylarsine: Evidence for the Formation of a T-Shaped Complex $[PhPdI(AsPh_3)]$ and for the Decelerating Effect of $CH_2{=}CH{-}SnBu_3$ by Formation of $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$

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**Abstract:** The oxidative addition of phenyl iodide to the palladium(0) generated from $[Pd^0(dba)_2]$ and $n$ equivalents of $AsPh_3$ (the most efficient catalytic precursor in Stille reactions) proceeds from $[(solv)Pd^0(AsPh_3)_2]$ (solv = solvent). However, the latter is present only in trace concentrations because it is involved in an equilibrium with the major, but nonreactive, complex $[Pd^0(dba)(AsPh_3)_2]$. As regards the phosphine ligands, dba has a decelerating effect on the rate of the oxidative addition by decreasing the concentration of the reactive species. Relative to $PPh_3$, the effect of $AsPh_3$ is to increase the rate of the oxidative addition of PhI by a factor ten in DMF and seven in THF, independent of the value of $n$, provided that $n \geq 2$. In contrast to $PPh_3$, the addition of more than two equivalents of $AsPh_3$ to $[Pd^0(dba)_2]$ (dba = *trans,trans*-dibenzylideneacetone) does not affect the kinetics of the oxidative addition because of the very endergonic displacement of dba from $[Pd^0(dba)(AsPh_3)_2]$ to form $[Pd^0(AsPh_3)_3]$. The complex *trans*-$[PhPdI(AsPh_3)_2]$, formed in the oxidative addition, is involved in a slow equilibrium with the T-shaped complex $[PhPdI(AsPh_3)]$ after appreciable decomplexation of one $AsPh_3$. Under catalytic conditions, that is, in the presence of a nucleophile, such as $CH_2{=}CH{-}SnBu_3$ which is able to coordinate to $[Pd^0(AsPh_3)_2]$, a new $Pd^0$ complex is formed: $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$; however, this complex does not react with PhI. Consequently, $CH_2{=}CH{-}SnBu_3$ slows down the oxidative addition by decreasing the concentration of the reactive species $[(solv)Pd^0(AsPh_3)_2]$. This demonstrates that a nucleophile may be not only involved in the transmetallation step, but may also interfere in the kinetics of the oxidative addition step by decreasing the concentration of reactive $Pd^0$.

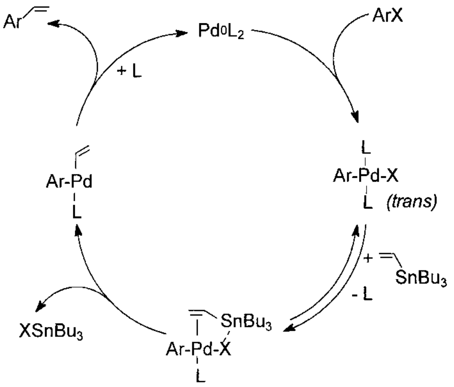
**Keywords:** As ligands · oxidative addition · palladium · reaction mechanisms · tin derivatives

## Introduction

It has been reported that there is a large rate acceleration in Stille reactions [Eq. (1)] with tri-2-furylphosphine (tfp) and triphenylarsine ($AsPh_3$) as palladium ligands, of two and three orders of magnitude, respectively, relative to $PPh_3$.[1, 2]

$$ArI + CH_2{=}CH{-}SnBu_3 \xrightarrow{Pd} Ar{-}CH{=}CH_2 + ISnBu_3 \qquad (1)$$

The mechanism, described in Scheme 1, involves three main steps: i) oxidative addition of a $[Pd^0L_2]$ complex to ArX to form *trans*-$[ArPdXL_2]$, ii) transmetallation of the nucleophile (vinyl)$SnBu_3$ with $[ArPdXL_2]$, and iii) reductive elimination from $[ArPd(vinyl)L]$.[1, 3] The transmetallation is the rate-determining step.[1, 3] It is affected by the ligand and is reported to proceed either by a dissociative[1] or an associative mechanism.[3]



Scheme 1. Mechanism of the Pd-catalyzed Stille reaction.

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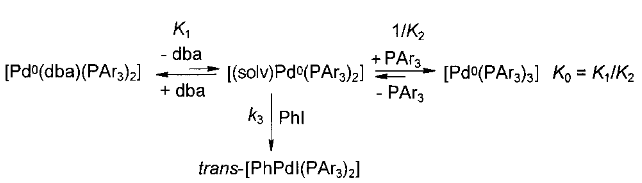
Although the oxidative addition with aryl iodides is not rate determining,[1, 3] it is of interest to investigate the effect of the ligand on this step, that is, i) to characterize the reactive $Pd^0$ species, ii) to measure its reactivity, iii) to characterize the arylpalladium(II) complex formed in the oxidative addition, since this complex is considered to react with the nucleophile, and iv) to investigate the mechanism of the oxidative addition in the presence of a nucleophile to test its possible influence on the kinetics of this reaction, whenever the nucleophile might be a ligand of the $Pd^0$, as, for example, $CH_2{=}CH{-}SnBu_3$.

We have reported a mechanistic investigation of the oxidative addition of PhI to the $Pd^0$ complex generated from $[Pd^0(dba)_2]$ (dba = *trans,trans*-dibenzylideneacetone)[4] associated with the tfp ligand[5] and established that the oxidative addition proceeds, as for $PPh_3$[6] and triarylphosphines $PAr_3$,[7] from the minor complex $[(solv)Pd^0(PAr_3)_2]$ (solv = solvent) in THF and DMF, whereas the major species is the unreactive complex $[Pd^0(dba)(PAr_3)_2]$ (Scheme 2, $K_0 < 0.5$ for tfp and $PPh_3$ in both solvents).[5]



Scheme 2. Oxidative addition of PhI to the $Pd^0$ complex generated from $[Pd^0(dba)_2]$ and $nPAr_3$ ($PAr_3 = PPh_3$, tfp; $n \geq 2$).

The following order of reactivity with PhI has been established in a previous work:[5]

In DMF: $[Pd^0(dba)_2] + n\,tfp > [Pd^0(dba)_2] + n\,PPh_3$ for all $n \geq 2$ equiv

In THF: $[Pd^0(dba)_2] + n\,tfp < [Pd^0(dba)_2] + n\,PPh_3$ when $6 > n \geq 2$ equiv

This relative order is perfectly coherent with the relative variation found for the rate constant $k_3$ of the oxidative addition step (which characterizes the reactivity of $[(solv)Pd^0(PAr_3)_2]$) and the relative variation of $K_1$ and $K_0$ (which control the $[(solv)Pd^0(PAr_3)_2]$ concentration) as a function of the ligand and solvent.[5] However, the difference in reactivity, when in favor of tfp, is too low to be at the origin of the large acceleration observed in Stille reactions with TPF as the palladium ligand instead of $PPh_3$.[1] These results are then in good agreement with the argument which assumes that transmetallation is the rate-determining step and that this step is strongly affected by the ligand.[1, 3]

We now report a mechanistic investigation of the oxidative addition of PhI to the $Pd^0$ complexes formed from $[Pd^0(dba)_2] + n\,AsPh_3$ ($n \geq 2$ equiv).[4, 8] The kinetics of the oxidative addition has also been investigated in the presence of a nucleophile, $CH_2{=}CH{-}SnBu_3$ (vinyltributyltin). Indeed, this nucleophile possesses a C=C bond able to coordinate a $Pd^0$ complex, as dba does, and might then affect the rate of the oxidative addition. This situation is then closer to the real catalytic conditions of a Stille reaction.

## Results and Discussion

**Identification of the palladium(0) complexes generated from $[Pd^0(dba)_2] + n\,AsPh_3$ ($n \geq 2$ equiv) in THF and DMF as investigated by cyclic voltammetry and UV spectroscopy**: The cyclic voltammogram of a solution of $[Pd^0(dba)_2]$ (2 mmol $dm^{-3}$) and $AsPh_3$ (2 equiv) in THF (containing $nBu_4NBF_4$, 0.3 mol $dm^{-3}$) exhibited one oxidation peak $O_1$ at $E_p = +0.83$ V (Figure 1a), whereas the oxidation peak of $[Pd^0(dba)_2]$ at +1.26 V was no longer detected. In reduction, the cyclic voltammogram exhibited three peaks $R_1$, $R_2$, $R_3$ at −1.30, −1.65 and −1.90 V, respectively (Figure 1b). The reductions peaks $R_1$ and $R_3$ characterize the free dba ligand at a concentration of 2 mmol $dm^{-3}$, as determined by comparison with the reduction peak currents of a sample of dba (2 mmol $dm^{-3}$) obtained under the same conditions (the currents were proportional to the concentrations of electroactive species). Therefore, as for phosphine ligands,[7] one dba remained ligated to the $Pd^0$ center. The oxidation peak $O_1$ and reduction peak $R_2$ characterize the complex $[Pd^0(dba)(AsPh_3)_2]$ formed in the reaction given in Equation (2).

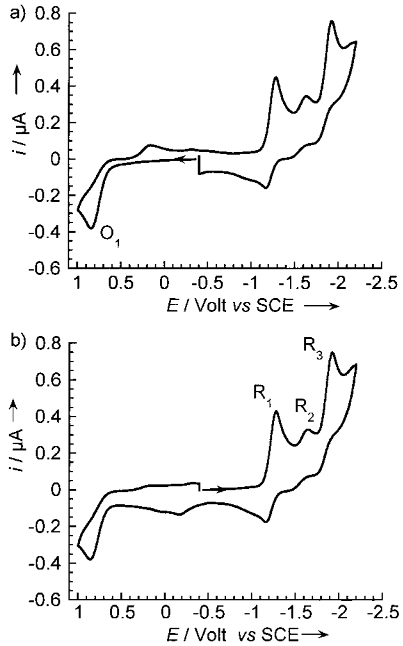


Figure 1. Cyclic voltammetry of a solution of $[Pd^0(dba)_2]$ (2 mmol $dm^{-3}$) and $AsPh_3$ (4 mmol $dm^{-3}$) in THF (containing $nBu_4NBF_4$, 0.3 mmol $dm^{-3}$) at a stationary gold-disk electrode (0.5 mm diameter) with a scan rate of 0.5 V $s^{-1}$. a) Oxidation first. b) Reduction first.

$$[Pd^0(dba)_2] + 2\,AsPh_3 \rightarrow [Pd^0(dba)(AsPh_3)_2] + dba \qquad (2)$$

$[Pd^0(dba)(AsPh_3)_2]$ was also characterized by its adsorption band at $\lambda = 387$ nm in THF or 394 nm in DMF; this band is characteristic of the dba ligated to $Pd^0$, as observed with phosphine ligands.[7, 9]

In contrast to $PPh_3$[6] or tfp,[5] for which the oxidation peak of the minor complex $[(solv)Pd^0(PAr_3)_2]$ was detected at less positive potential than the oxidation potential of [Pd⁰(dba)-

$(PAr_3)_2]$, the oxidation peak of $[(solv)Pd^0(AsPh_3)_2]$ was not observed, although a kinetic investigation of the oxidative addition of PhI (vide infra) gave clear kinetic evidence for the involvement of $[(solv)Pd^0(AsPh_3)_2]$ as the reactive species. This shows that the equilibrium [Eq. (3)] lies more in favor of $[Pd^0(dba)(AsPh_3)_2]$ or/and is less labile than in the corresponding equilibria where $PPh_3$[6] or tfp[5] are palladium ligands (Scheme 2); therefore, $K_1(AsPh_3) < K_1(PPh_3) < K_1(tfp)$.

$$[Pd^0(dba)(AsPh_3)_2] \xrightleftharpoons{K_1} [(solv)Pd^0(AsPh_3)_2] + dba \tag{3}$$

In the presence of more than two equivalents of $AsPh_3$ per $[Pd^0(dba)_2]$ (however, $n$ is limited to $n = 10$ because of the low solubility of $AsPh_3$ in THF), the UV spectrum of $[Pd^0(dba)(AsPh_3)_2]$ was not modified. This indicates that, in contrast to $PPh_3$ and tfp (Scheme 2), the dba ligand of $[Pd^0(dba)(AsPh_3)_2]$ is not significantly displaced by $AsPh_3$ to yield $[Pd^0(AsPh_3)_3]$ [Eq. (4)].

$$[Pd^0(dba)(AsPh_3)_2] + AsPh_3 \xrightleftharpoons{K_0} [Pd^0(AsPh_3)_3] + dba \tag{4}$$

However, on the cyclic voltammogram that exhibits the oxidation peak $O_1$ of $[Pd^0(dba)(AsPh_3)_2]$, a new oxidation wave $O_2$ was observed at a less positive potential (Figure 2), after the addition of $AsPh_3$. When the scan rate was decreased, there was a relative increase in the oxidation current of $O_2$ compared to that of $[Pd^0(dba)(AsPh_3)_2]$ at $O_1$, (Figure 2a–c). This phenomenon, associated with the plateau-shaped form of $O_2$, is characteristic of a CE mechanism.[6] This establishes that $[Pd^0(AsPh_3)_3]$ (oxidized at $O_2$) is effectively formed [Eq. (4)], but at a thermodynamic very low concentration. However, it can be detected by cyclic voltammetry performed at low scan rates (i.e., on long timescales) because the equilibrium is then continuously displaced towards $[Pd^0(AsPh_3)_3]$, because of the consumption of $[Pd^0(AsPh_3)_3]$ by oxidation at $O_2$. The oxidation current is then proportional to the dynamic concentration of $[Pd^0(AsPh_3)_3]$. Whereas $K_0(PPh_3)$ (0.23 in THF; 0.14 in DMF) and $K_0$(tfp) (0.26 in THF; 0.32 in DMF) have been determined by UV spectroscopy,[5] the value of $K_0(AsPh_3)$ [Eq. (4)] is too low to be determined by this technique. The value of $K_0(AsPh_3)$ is only estimated. In the presence of ten equivalents of $AsPh_3$, $[Pd^0(AsPh_3)_3]/[Pd^0(dba)(AsPh_3)_2] \ll 0.05$, then $K_0(AsPh_3) \ll 5 \times 10^{-3}$. Consequently, $K_0(AsPh_3) \ll K_0(PPh_3) < K_0(tfp)$ in THF and DMF (Table 1).

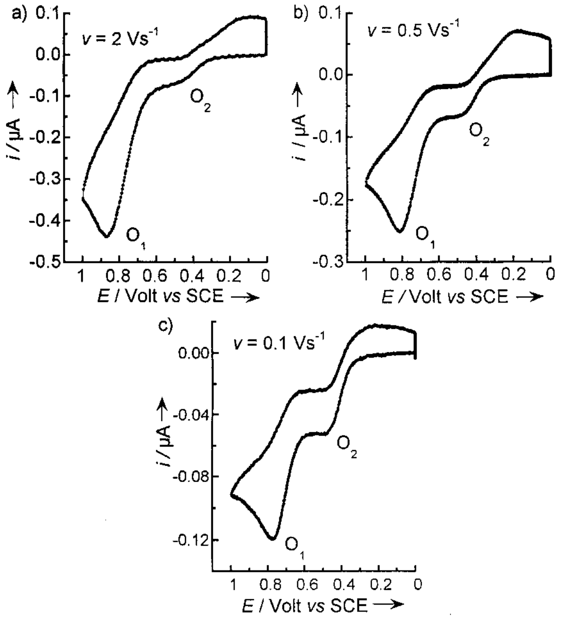


Figure 2. Cyclic voltammetry of a solution of $[Pd^0(dba)_2]$ ($2\,mmol\,dm^{-3}$) and $AsPh_3$ ($20\,mmol\,dm^{-3}$) in THF (containing $nBu_4NBF_4$, $0.3\,mmol\,dm^{-3}$) at a stationary gold-disk electrode (0.5 mm diameter) with different scan rates. a) $2\,V\,s^{-1}$, b) $0.5\,V\,s^{-1}$, c) $0.1\,V\,s^{-1}$. $O_1$: oxidation of $[Pd^0(dba)(AsPh_3)_2]$; $O_2$: oxidation of $[Pd^0(AsPh_3)_3]$.

Table 1. Equilibrium constants and kinetic parameters for the oxidative addition of PhI to the palladium(0) complexes generated from $[Pd^0(dba)_2]$ and $n$L ($n \geq 2$) according to Scheme 2 (for $PPh_3$)[6] and Scheme 3 (for $AsPh_3$).

| Ligand | Solvent | $T$[°C] | $10^2 \times k_3K_1\,[s^{-1}]$ | $10^2 \times k_3K_2\,[s^{-1}]$ | $K_0$ |
|---|---|---|---|---|---|
| $PPh_3$ | DMF | 20 | $0.63 \pm 0.01$ | $4.6 \pm 0.4$ | $0.14 \pm 0.03$ |
| $AsPh_3$ | DMF | 20 | $6.6 \pm 0.1$ | – | $\ll 5 \times 10^{-3}$ |
| $PPh_3$ | THF | 20 | $1.10 \pm 0.01$ | $4.7 \pm 0.1$ | $0.23 \pm 0.03$ |
| $AsPh_3$ | THF | 20 | $7.8 \pm 0.1$ | – | $\ll 5 \times 10^{-3}$ |
| $AsPh_3$ | THF | 28 | 17 | – | – |

As seen above, in contrast to $PPh_3$ and tfp, the 14-electron complex $[(solv)Pd^0(AsPh_3)_2]$ cannot be detected in the mixture $[Pd^0(dba)_2] + 2\,AsPh_3$. Its thermodynamic concentration in the equilibrium in Equation (3) is considerably lower than that of $[(solv)Pd^0(PPh_3)_2]$ or $[(solv)Pd^0(tfp)_2]$ in the corresponding equilibria. Therefore, dba is a much better ligand for $[Pd^0(AsPh_3)_2]$ than for $[Pd^0(PPh_3)_2]$ or $[Pd^0(tfp)_2]$. In the presence of excess $AsPh_3$ ($n > 2$), the complex $[Pd^0(AsPh_3)_3]$ is only formed at trace concentration. The dba ligand in $[Pd^0(dba)(AsPh_3)_2]$ is then considerably less easily displaced by $AsPh_3$ [Eq. (4)] than for $PPh_3$ and tfp. This confirms the strong affinity of dba for $[Pd^0(AsPh_3)_2]$. Since $AsPh_3$ and $PPh_3$ have a very similar cone angle (142 and 145°, respectively),[10] this is certainly related to electronic parameters. However, to our knowledge, the latter remain unknown for $AsPh_3$.

**Rate and mechanism of the oxidative addition of PhI to the palladium(0) generated from $[Pd^0(dba)_2] + n\,AsPh_3$ ($n \geq 2$) in THF and DMF. Comparative reactivity with $PPh_3$:** In the previous papers of this series, the mechanism of the oxidative addition of PhI was established for $PPh_3$[6] and tfp,[5] and the reactive species identified as $[(solv)Pd^0(PAr_3)_2]$ (Scheme 2). As already reported, the reactivity of $Pd^0$ complexes in oxidative addition can be monitored by amperometry at a rotating-disk electrode (polarized at +0.8 V on the plateau of the oxidation wave of $[Pd^0(dba)(AsPh_3)_2]$) as a function of time.[6] This takes advantage of the fact that the oxidation current $i$ of the $Pd^0$ remains proportional to its concentration during the oxidative addition of PhI. A second analytical technique at hand is provided by UV spectroscopy,[9] since [Pd$^0$(dba)(AsPh$_3$)$_2$] exhibits an absorption band which disappears in the presence of excess PhI. Both techniques give similar results.[9]

*Identification of the reactive species generated from [Pd$^0$(dba)$_2$] + AsPh$_3$ (2 equiv) in THF and DMF*: When the oxidative addition was performed in the presence of excess dba (10 equiv, 20 mM) and excess PhI, the plot of ln($i/i_0$) = ln([Pd$^0$]/[Pd$^0$]$_0$) versus time was linear (Figure 3a) ($i$: oxidation peak current at O$_1$ at $t$, $i_0$: initial oxidation peak current at O$_1$). This shows that the reaction order in Pd$^0$ is +1. The slope of the regression line, ln[Pd$^0$]/[Pd$^0$]$_0$ = −$k_{exp}t$, gave the value of the observed rate constant $k_{exp}$. The latter varied linearly with PhI concentration (Figure 3b), showing that the reaction order in PhI is +1. The reaction with five equivalents of PhI was slower when the dba concentration was increased. The observed rate constant $k_{exp}$ was determined by UV spectroscopy from a plot of 0.25 ln[(4 + $x$)/5$x$] versus time (Figure 4a) ($x$ = [Pd$^0$]/[Pd$^0$]$_0$ = ($D - D_\infty$)/($D_0 - D_\infty$); $D$: absorbance at $t$; $D_\infty$ absorbance at $t_\infty$; $D_0$: initial absorbance). Thus 0.25 ln[(4 + $x$)/5$x$] = $k_{exp}t$.[6] The value of 1/$k_{exp}$ varied linearly with the dba concentration (Figure 4b), showing that the reaction order in dba is −1.

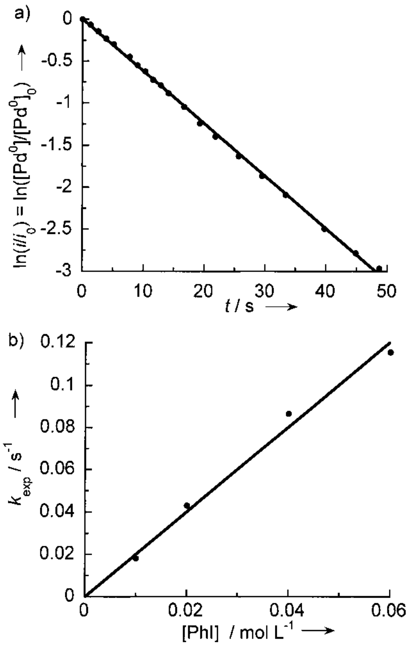


Figure 3. Kinetics of the oxidative addition of PhI to the palladium(0) complex generated from [Pd$^0$(dba)$_2$] (2 mmol dm$^{-3}$) and AsPh$_3$ (4 mmol dm$^{-3}$) in THF (containing $n$Bu$_4$NBF$_4$, 0.3 mmol dm$^{-3}$) at 28 °C, monitored by amperometry at a rotating gold-disk electrode (i.d. 2 mm, $\vartheta = 105$ rad s$^{-1}$). a) Kinetics performed in the presence of PhI (20 mmol dm$^{-3}$) and dba (20 mmol dm$^{-3}$). Plot of ln($i/i_0$) = ln([Pd$^0$]/[Pd$^0$]$_0$) versus time ($i$: oxidation current of [Pd$^0$(dba)AsPh$_3$)$_2$] at $t$, $i_0$: initial oxidation current of [Pd$^0$(dba)(AsPh$_3$)$_2$]), ln[Pd$^0$]/[Pd$^0$]$_0$ = −$k_{exp}t$. b) Variation of $k_{exp}$ versus PhI concentration in the presence of dba (41 mmol dm$^{-3}$).

This establishes that the oxidative addition does not proceed from the major complex [Pd$^0$(dba)(AsPh$_3$)$_2$], but from the minor complex, [(solv)Pd$^0$(AsPh$_3$)$_2$] (Scheme 3). Both complexes are involved in a fast equilibrium with dba, displaced by the slower oxidative addition step. Once again dba plays an important role by controlling the concentration of the reactive complex, although the effective oxidative addition step does not involve a dba-ligated Pd$^0$ species.[7]

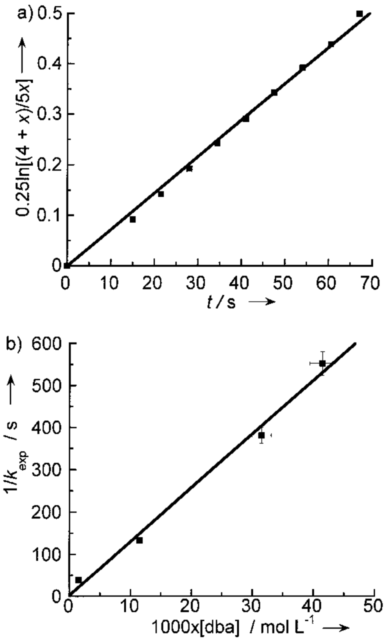
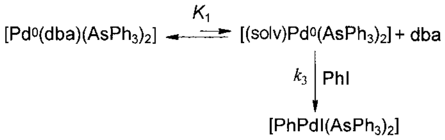


Figure 4. Kinetics of the oxidative addition of PhI (5 mmol dm$^{-3}$) to the palladium(0) complex generated from [Pd$^0$(dba)$_2$] (1 mmol dm$^{-3}$) and AsPh$_3$ (2 mmol dm$^{-3}$) in THF at 20 °C, monitored by UV spectroscopy. a) Plot of 0.25 ln[(4 + $x$)/5$x$] versus time ($x$ = [Pd$^0$]/[Pd$^0$]$_0$ = ($D - D_\infty$)/($D_0 - D_\infty$); $D$: absorbance of [Pd$^0$(dba)(AsPh$_3$)$_2$] at $t$; $D_\infty$ absorbance at $t_\infty$; $D_0$: initial absorbance); 0.25 ln[(4 + $x$)/5$x$] = $k_{exp}t$. b) Variation of 1/$k_{exp}$ versus 1/[dba].



Scheme 3. Oxidative addition of PhI to the Pd$^0$ complex generated from [Pd$^0$(dba)$_2$] and $n$ equivalents of AsPh$_3$ ($n \geq 2$).

In contrast to what was observed for PPh$_3$[6] and tfp,[5] the rate of the oxidative addition was not affected by addition of increasing amounts of AsPh$_3$ to the mixture [Pd$^0$(dba)$_2$] + AsPh$_3$ (2 equiv). The concentration of the active species, [(solv)Pd$^0$(AsPh$_3$)$_2$], is, therefore, not controlled by the AsPh$_3$ concentration. This is in agreement with the small value of $K_0$(AsPh$_3$) [Eq. (4)] estimated above. Consequently, whatever $n \geq 2$, the mechanism of the oxidative addition is described in Scheme 3, without any significant contribution of the equilibrium between [Pd$^0$(AsPh$_3$)$_3$] and [(solv)Pd$^0$(AsPh$_3$)$_2$], in contrast to PPh$_3$[6] or tfp[5] (Scheme 2). The overall oxidative addition is thus only controlled by the values of $k_3$, $K_1$, and the dba concentration (Scheme 3). The value of $k_3K_1$ (Table 1) was determined from the slope of the regression line of Figure 4b. Indeed, according to the mechanism of Scheme 3, the rate law is: 0.25 ln[(4 + $x$)/5$x$] = $k_{exp}t = k_3K_1C_0t$/[dba].[6]

The overall reactivity of [Pd$^0$(dba)$_2$] + AsPh$_3$ (2 equiv) is then found higher than that of [Pd$^0$(dba)$_2$] + PPh$_3$ (2 equiv),[6] $k_3$(AsPh$_3$)$K_1$(AsPh$_3$) > $k_3$(PPh$_3$)$K_1$(PPh$_3$) whatever the solvent, THF or DMF (Table 1). Since $K_1$(AsPh$_3$) < $K_1$(PPh$_3$) (vide supra), this implies that $k_3$(AsPh$_3$) ≫ $k_3$(PPh$_3$). Even if the concentration of [(solv)Pd$^0$(AsPh$_3$)$_2$] is smaller than that of [(solv)Pd$^0$(PPh$_3$)$_2$], its intrinsic reactivity in the oxidation step is much higher and as a result of these two antagonist effects, the system involving AsPh$_3$ is more reactive than that involving PPh$_3$. In the absence of available data on the comparative basicity of AsPh$_3$ and PPh$_3$, it is usually considered that AsPh$_3$ is a less effective σ-donor but a better π-acceptor than PPh$_3$. It is then deduced that a Pd$^0$ complex ligated by AsPh$_3$ is intrinsically less reactive than a Pd$^0$ complex ligated by PPh$_3$. Our results establish the opposite order: $k_3$(AsPh$_3$) > $k_3$(PPh$_3$).

Therefore, the system involving AsPh$_3$ is more reactive than that involving PPh$_3$ by an overall factor of ten in DMF and seven in THF. However, this difference in reactivity is too low to be at the origin of the large acceleration (by a factor of $10^3$) observed in Stille reactions of PhI with AsPh$_3$ as the ligand instead of PPh$_3$.[1] This confirms that the accelerating effect is not result of the oxidative addition but of the further transmetallation step, as established by Farina and Krishnan,[1] Casado and Espinet.[3]

**Characterization of the Pd$^{II}$ complex formed in the oxidative addition**: The phenylpalladium(II) complex formed in the oxidative addition of PhI to the Pd$^0$ complex generated from [Pd$^0$(dba)$_2$] and two equivalents of AsPh$_3$ has been isolated and characterized by $^1$H NMR spectroscopy in CDCl$_3$ (Figure 5a). One observes three signals at $\delta = 6.72$ (d, $J = 7$ Hz, 2H; $o$-H), 6.47 (t, $J = 7$ Hz, 1H; $p$-H), 6.37 (t, $J = 7$ Hz, 2H; $m$-H) that are characteristic of a phenyl linked to a Pd$^{II}$, as in the *trans*-[PhPdI(PPh$_3$)$_2$] complex.[11] These signals were then assigned to *trans*-[PhPdI(AsPh$_3$)$_2$]. Another unusual set of three signals at $\delta = 7.13$ (d, $J = 7$ Hz, 2H; $o$-H), 6.68 (t, 2H; $m$-H), 6.65 (t, 1H; $p$-H) were also detected. They belong to a single phenyl group, as established from a COSY experiment (Figure 5a). This shows that a second phenylpalladium(II) complex is formed together with *trans*-[PhPdI(AsPh$_3$)$_2$]. The formation of a cationic complex *trans*-[PhPd(solv)(AsPh$_3$)$_2$]$^+$, which could be involved in an equilibrium with *trans*-[PhPdI(AsPh$_3$)$_2$],[12a] was ruled out since a solution of *trans*-[PhPdI(AsPh$_3$)$_2$] (2 mmol dm$^{-3}$ in DMF) did not exhibit any significant conductivity (2.5 μS).[13] Furthermore, after addition of AsPh$_3$, the unusual set of three signals disappeared and only those that featured *trans*-[PhPdI(AsPh$_3$)$_2$] could be detected. These $^1$H NMR experiments establish unambiguously that the main complex *trans*-[PhPdI(AsPh$_3$)$_2$] is involved in an equilibrium with AsPh$_3$ and a second phenylpalladium(II) complex, which is presumably the so-called T-shaped complex [PhPdI(solv)(AsPh$_3$)][14] (Scheme 4), as evidenced by Farina from kinetic investigations.[1, 2]

The equilibrium constant: $K_L$ = [PhPdI(solv)(AsPh$_3$)] × [AsPh$_3$]/[PhPdI(AsPh$_3$)$_2$] (Scheme 4) was then determined from the respective integration of the $^1$H NMR signals of *trans*-[PhPdI(AsPh$_3$)$_2$] and [PhPdI(solv)(AsPh$_3$)]: $K_L/C_0 = 0.07$ in CDCl$_3$ at 20 °C (22 % dissociation).

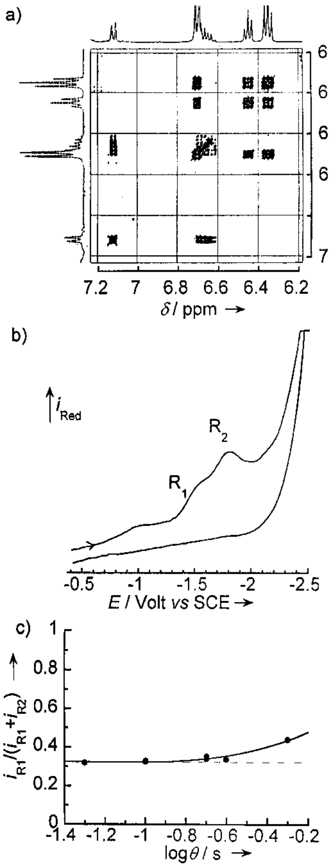
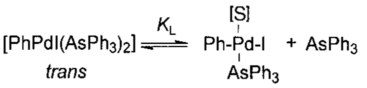


Figure 5. Characterization of the complexes formed in the oxidative addition of PhI to the palladium(0) complex generated from [Pd$^0$(dba)$_2$] and two equivalents of AsPh$_3$. a) COSY experiment on [PhPdI(AsPh$_3$)$_2$] in CDCl$_3$ (400 MHz, TMS). b) Cyclic voltammetry of a solution of [PhPdI(AsPh$_3$)$_2$] (2 mmol dm$^{-3}$) in DMF (containing $n$Bu$_4$NBF$_4$, 0.3 mmol dm$^{-3}$) at a stationary gold-disk electrode (0.5 mm diameter) with a scan rate of 0.2 V s$^{-1}$; R$_1$: reduction wave of [PhPdI(solv)(AsPh$_3$)]; R$_2$: reduction wave of *trans*-[PhPdI(AsPh$_3$)$_2$]. c) Determination of the equilibrium constant $K_L$ between [PhPdI(solv)(AsPh$_3$)] and *trans*-[PhPdI(AsPh$_3$)$_2$] (Scheme 4) by chronoamperometry performed at a stationary gold-disk electrode (0.5 mm diameter). Plot of $i_{R1}/(i_{R1} + i_{R2})$ versus log θ (θ: duration of the potential step of the chronoamperometry).



$$\underset{trans}{[\mathrm{PhPdI(AsPh_3)_2}]} \overset{K_L}{\rightleftharpoons} \mathrm{Ph\text{-}}\overset{[S]}{\underset{\mathrm{AsPh_3}}{\mathrm{Pd}}}\mathrm{\text{-}I} + \mathrm{AsPh_3}$$

Scheme 4. Equilibrium between [PhPdI(AsPh$_3$)$_2$] and the T-shaped complex [PhPdI(solv)(AsPh$_3$)] ([S] = solvent).

The T-shaped complex [PhPdI(solv)(AsPh$_3$)] was also characterized by cyclic voltammetry performed in DMF (containing $n$Bu$_4$NBF$_4$, 0.3 mol dm$^{-3}$). The voltammogram of a solution of *trans*-[PhPdI(AsPh$_3$)$_2$] (2 mM) at 0.2 V s$^{-1}$ exhibited two successive irreversible reduction peaks, R$_1$ and R$_2$ at −1.58 and −1.76 V, respectively, versus SCE (Figure 5b). The reduction current of R$_1$ decreased after addition of AsPh$_3$, whereas the reduction current of R$_2$ increased. This indicates that R$_1$ characterizes [PhPdI(solv)(AsPh$_3$)], whereas R$_2$ characterizes *trans*-[PhPdI(AsPh$_3$)$_2$]. The ratio of the two reduction currents at short times, which reflects the ratio of their respective concentration at equilibrium, has been determined by chronoamperometry.[12b] The plot of $i_{R1}/(i_{R1} + i_{R2})$ versus $\log\theta$ ($\theta$: duration of the potential step of the chronoamperometry) is shown in Figure 5c. The equilibrium is frozen at the shortest times investigated ($50 < \theta < 100$ ms), as evidenced by the constant value of $i_{R1}/(i_{R1} + i_{R2})$ in this time range (Figure 5c). This constant value gives the thermodynamic concentration of [PhPdI(solv)(AsPh$_3$)] in the equilibrium and provides the equilibrium constant $K_L$ (Scheme 4). Thus $K_L = 3 \times 10^{-4}$ mol L$^{-1}$ in DMF at 25 °C and $K_L/C_0 = 0.15$ ($C_0 = 2$ mM)

This corresponds to 32 % dissociation under the conditions of Figure 5c. The equilibrium is not very labile since times of $\theta > 0.5$ s are required to shift the equilibrium, as indicated by the slow increase of $i_{R1}/(i_{R1} + i_{R2})$ above this time (Figure 5 c).

To our knowledge, this is the first spectroscopic evidence for the formation of the so-called T-shaped complex. Its formation has been deduced by Farina and Roth[2] from kinetic investigations, with a value of $K_L = 8.6 \times 10^{-4}$ mol L$^{-1}$ in THF at 50 °C, which corresponds to $K_L/C_0 = 0.27$ (40 % dissociation). All $K_L$ values are coherent and establish the presence of the T-shaped complex [PhPdI(solv)(AsPh$_3$)] in appreciable concentration. The formation of transient intermediate T-shaped [ArPdBr(PPh$_3$)] complexes has been also established by Louie and Hartwig,[15] from kinetic investigations on the reaction of *trans*-[ArPdBr(PPh$_3$)$_2$] complexes with organostannanes, for example, PhSnBu$_3$.

**Influence of CH$_2$=CH−SnBu$_3$ on the rate and mechanism of the oxidative addition of PhI to the palladium(0) generated from [Pd$^0$(dba)$_2$] + AsPh$_3$ (2 equiv) in THF and DMF**: The influence of a nucleophile, such as CH$_2$=CH−SnBu$_3$, on the mechanism of the oxidative addition of PhI has been investigated. Indeed, this nucleophile possesses a C=C double bond and might be a ligand of the Pd$^0$. Consequently, a competition might exist between dba and CH$_2$=CH−SnBu$_3$ for the complexation of the [Pd$^0$(AsPh$_3$)$_2$] moiety. A competition which will be enhanced by the considerably higher concentration of CH$_2$=CH−SnBu$_3$ compared to that of dba, in a true catalytic reaction. Moreover, it has been recently reported that PhC≡C−SnBu$_3$ undergoes oxidative addition to Pd$^0$ complexes through activation of its C−Sn bond.[16] It is thus of great interest to determine the mechanism of the oxidative addition of PhI in the presence of CH$_2$=CH−SnBu$_3$.

*Evidence for the formation of [Pd$^0$($\eta^2$-CH$_2$=CH−SnBu$_3$)(AsPh$_3$)$_2$]*: When the UV spectroscopy of the complex [Pd$^0$(dba)(AsPh$_3$)$_2$] (1 mmol dm$^{-3}$), formed quantitatively from [Pd$^0$(dba)$_2$] and AsPh$_3$ (2 equiv) in DMF and THF, was performed in the presence of excess CH$_2$=CH−SnBu$_3$, one observed a rapid partial decay of its absorbance (Figure 6a). This limiting value decreased again after successive additions of CH$_2$=CH−SnBu$_3$ (Figure 6a) and increased after addition of dba. This indicates that [Pd$^0$(dba)(AsPh$_3$)$_2$] and CH$_2$=CH−SnBu$_3$ are involved in an equilibrium, whereas dba plays a role in the reverse reaction. Since oxidative addition of Pd$^0$ complexes are usually irreversible, the observed reaction is certainly not an oxidative addition of CH$_2$=CH−SnBu$_3$ to [(solv)Pd$^0$(AsPh$_3$)$_2$] by activation of the C−Sn bond, but rather a reversible complexation of [Pd$^0$(AsPh$_3$)$_2$] by CH$_2$=CH−SnBu$_3$ [Eq. (5)]. This is also supported by the fact that no reaction was observed when a noncomplexing organostannane, such as Ph−SnBu$_3$, was added to a solution of [Pd$^0$(dba)(AsPh$_3$)$_2$] in THF.

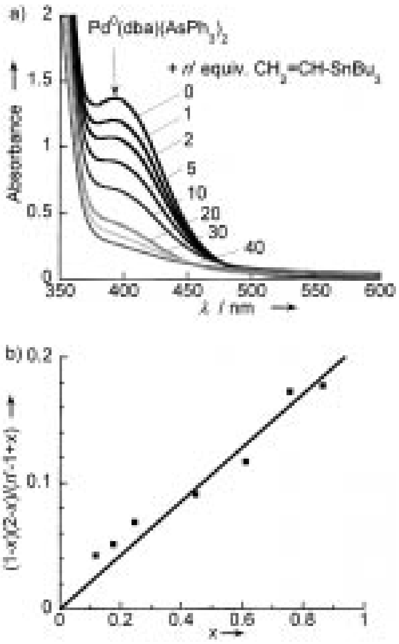
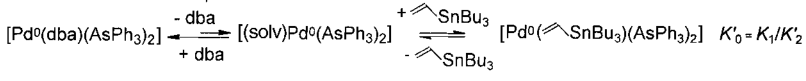


Figure 6. a) UV spectrum of a solution of [Pd$^0$(dba)$_2$] (1 mmol dm$^{-3}$) and AsPh$_3$ (2 mmol dm$^{-3}$) in DMF in a 1 mm path cell in the presence of $n'$ equiv of CH$_2$=CH−SnBu$_3$. b) Determination of the equilibrium constant $K'_0$ between [Pd$^0$(dba)(AsPh$_3$)$_2$] and [Pd$^0$(CH$_2$=CH−SnBu$_3$)(AsPh$_3$)$_2$] [Eq. (5)] at 20 °C. Plot of $(1-x)(2-x)/(n'-1+x)$ versus $x$ ($x = [Pd^0(dba)(AsPh_3)_2]_{equil}/[Pd^0(dba)(AsPh_3)_2]_0 = (D - D_\infty)/(D_0 - D_\infty)$; $D$: absorbance at equilibrium; $D_\infty$ absorbance when the equilibrium was totally shifted towards [Pd$^0$($\eta^2$-CH$_2$=CH−SnBu$_3$)(AsPh$_3$)$_2$], $D_0$: initial absorbance). $(1-x)(2-x)/(n'-1+x) = K'_0x$.

$$[Pd^0(dba)(AsPh_3)_2] + CH_2{=}CH{-}SnBu_3 \overset{K'_0}{\rightleftarrows} [Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2] + dba \quad (5)$$

In Equation (5) $K'_0 = [Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2] \times [dba]/[CH_2{=}CH{-}SnBu_3][Pd^0(dba)(AsPh_3)_2]$. The equilibrium is an overall equilibrium which results from two successive equilibria (Scheme 5).

Cyclic voltammetry of a solution of [Pd$^0$(dba)(AsPh$_3$)$_2$] (2 mmol dm$^{-3}$ in THF) in the presence of increasing amounts of CH$_2$=CH−SnBu$_3$ (by 10 equiv at a time) showed in the successive decay of the oxidation peak current of [Pd$^0$(dba)(AsPh$_3$)$_2$]. This is further evidence for the establishment of the equilibrium given in Equation (5). However, no new oxidation peak appeared which featured an oxidation of



Scheme 5. Equilibrium between Pd$^0$ complexes ligated by AsPh$_3$ and/or dba, CH$_2$=CH−SnBu$_3$.

$[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$.[17] Therefore, this last complex is much less oxidizable than $[Pd^0(dba)(AsPh_3)_2]$.

The equilibrium constant $K'_0$ [Eq. (5)] was determined in DMF and THF by UV spectroscopy which provided the thermodynamic concentration of $[Pd^0(dba)(AsPh_3)_2]$ in the equilibrium as a function of the $CH_2{=}CH{-}SnBu_3$ concentration. The plot of $(1-x)(2-x)/(n'-1+x)$ versus $x$ was linear (Figure 6b) ($n'$ = equiv of $CH_2{=}CH{-}SnBu_3$, $x = [Pd^0(dba)(AsPh_3)_2]_{equil}/[Pd^0(dba)(AsPh_3)_2]_0 = (D - D_\infty)/(D_0 - D_\infty)$; $D$: absorbance at equilibrium; $D_\infty$ absorbance when the equilibrium was totally shifted towards $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$, $D_0$: initial absorbance). $K'_0$ was then determined from the slope of the regression line (Figure 6b, Table 2) to be $(1-x)(2-x)/(n'-1+x) = K'_0x$.

Table 2. Equilibrium constant $K'_0$ between $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$ and $[Pd^0(dba)(AsPh_3)_2]$, generated from $[Pd(dba)_2]$ and two equivalents of $AsPh_3$, in THF and DMF [Eq. (5), Scheme 5]. Comparison with $PPh_3$.

| Ligand | Solvent | $T$[°C] | $K'_0$ |
|---|---|---|---|
| $AsPh_3$ | DMF | 20 | $0.21 \pm 0.01$[a] |
| $AsPh_3$ | THF | 20 | $0.06 \pm 0.02$[a] |
| $AsPh_3$ | THF | 28 | $0.036 \pm 0.002$[b] |
| $PPh_3$ | THF | 28 | 0.0001[a] |

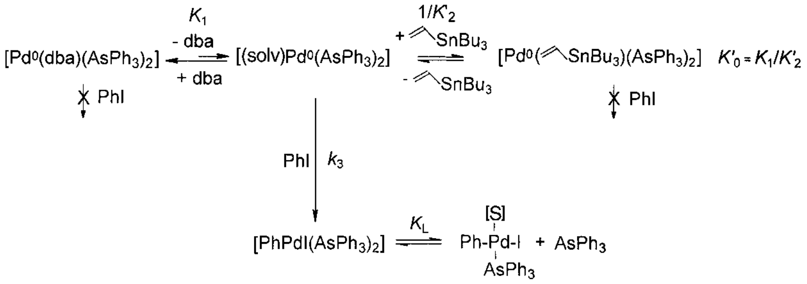
[a] Determined from UV spectroscopic data. [b] Determined from the kinetics.

For comparable concentrations of dba and $CH_2{=}CH{-}SnBu_3$, the affinity of $CH_2{=}CH{-}SnBu_3$ for the $[Pd^0(AsPh_3)_2]$ moiety is then smaller than that of dba. However, under catalytic conditions, $CH_2{=}CH{-}SnBu_3$ is in large excess relative to dba. When $[CH_2{=}CH{-}SnBu_3]/[dba] = 50$,[1] the ratio $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]/[Pd^0(dba)(AsPh_3)_2]$ may be calculated from the value of $K'_0 = 0.21$ in DMF, and is found to be ≈10. This means that the overall equilibrium lies more in favor of $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$ under realistic catalytic conditions.

A similar complexation of $CH_2{=}CH{-}SnBu_3$ to $[Pd^0(PPh_3)_2]$ to form $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(PPh_3)_2]$ occurred upon addition of $CH_2{=}CH{-}SnBu_3$ to $[Pd^0(dba)_2]$ and two equivalents of $PPh_3$ in THF. The determination of $K'_0$ for $PPh_3$ (Table 2) shows that the overall equilibrium in Scheme 5 lies more in favor of $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$ than for $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(PPh_3)_2]$ ($K'_0(AsPh_3) \gg K'_0(PPh_3)$). Since $K_1(AsPh_3) < K_1(PPh_3)$ (vide supra), this means that $K'_2(AsPh_3) \ll K'_2(PPh_3)$. In other words, the affinity of $CH_2{=}CH{-}SnBu_3$ for the $[Pd^0(AsPh_3)_2]$ moiety is considerably higher than that for the $[Pd^0(PPh_3)_2]$ moiety.

*Rate and mechanism of the oxidative addition of PhI in the presence of $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$. Determination of the reactive species in DMF and THF*: The oxidative addition of PhI to the $Pd^0$ complex, generated from $[Pd^0(dba)_2]$ (1 mM) and two equivalents of $AsPh_3$, was investigated in the presence of $CH_2{=}CH{-}SnBu_3$ at various concentrations in DMF and THF. The kinetics were monitored by UV spectroscopy. A preliminary check was made under our experimental conditions to make sure that the formation of styrene by the cross-coupling reaction was much slower than the oxidative addition, so that the regeneration of the $Pd^0$ complex by the cross-coupling reaction did not interfere significantly on the timescale of the oxidative addition. The oxidative addition of PhI was increasingly slower when the concentration of $CH_2{=}CH{-}SnBu_3$ was increased. This suggests that $[(solv)Pd^0(AsPh_3)_2]$ remains the reactive species in the presence of $CH_2{=}CH{-}SnBu_3$ (Scheme 6).

Indeed, the effect of $CH_2{=}CH{-}SnBu_3$ is to decrease the concentration of the reactive species $[(solv)Pd^0(AsPh_3)_2]$ by displacing the second equilibrium (equilibrium constant $1/K'_2$) towards the formation of the unreactive complex, $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$. If this last complex were the reactive species, increasing the $CH_2{=}CH{-}SnBu_3$ concentration would have resulted in an increase of the overall rate. Therefore, these results establish unambiguously that even if $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$ is the major $Pd^0$ complex in the presence of excess $CH_2{=}CH{-}SnBu_3$, the oxidative addition still proceeds via $[(solv)Pd^0(AsPh_3)_2]$ (Scheme 6).



Scheme 6. Mechanism of the oxidative addition of PhI to the $Pd^0$ complex generated from $[Pd^0(dba)_2]$ and $n$ equivalents of $AsPh_3$, ($n \geq 2$), in the presence of $CH_2{=}CH{-}SnBu_3$ ([S] = solvent).

The apparent rate constant $k_{app}$ of the oxidative addition, when performed in the presence of excesses of dba and $CH_2{=}CH{-}SnBu_3$, is then given by Equations (6) and (7)[18] (for simplification, $[CH_2{=}CH{-}SnBu_3]$ is designated as [Sn]).

$$\frac{1}{k_{app}[Sn]} = \frac{1}{k_3[Sn]} + \frac{1}{k_3K'_2[Sn]} + \frac{[dba]}{k_3K_1[Sn]} \tag{6}$$

$$\frac{1}{k_{app}[Sn]} = \frac{1}{k_3[Sn]} + \frac{1}{k_3K_1}\left(K'_0 + \frac{[dba]}{[Sn]}\right) \tag{7}$$

If the dba and $CH_2{=}CH{-}SnBu_3$ concentrations are too high, the oxidative addition will be very slow with the problem that the timescales of the oxidative addition (reaction order −1 in $CH_2{=}CH{-}SnBu_3$ and dba) and of the transmetallation (reaction order +1 in $CH_2{=}CH{-}SnBu_3$)[1–3] will become close. Under such conditions, there might be a possible interference in the oxidative addition of the $Pd^0$ regenerated in the sequence transmetallation/reductive elimination (Scheme 1).

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This is why the kinetics of the oxidative addition of PhI has been investigated from $[Pd^0(dba)_2]$ and two equivalent $AsPh_3$, without added dba, for $CH_2{=}CH{-}SnBu_3$ concentrations in the range 1–10 mmol dm$^{-3}$, or at low concentrations of dba (8 mmol dm$^{-3}$) and for $CH_2{=}CH{-}SnBu_3$ concentrations in the range 1–20 mmol dm$^{-3}$. The plot of $1/k_{app}[Sn]$ versus $K'_0$ + [dba]/[Sn] [Eq. (7)], with the value of $K'_0$ determined by UV spectroscopy (Table 2) was linear in DMF (Figure 7) and passed through zero. Then, $1/k_3[Sn] \ll 1$ and $k_3 \gg 10^3\,M^{-1}s^{-1}$. The value of $k_3K_1$ was determined from the slope of the regression line. This allows a second determination of $k_3K_1$: 0.19 instead of 0.066 in DMF (Table 1) and 0.068 instead of 0.078 in THF at 20 °C (Table 1).[19]

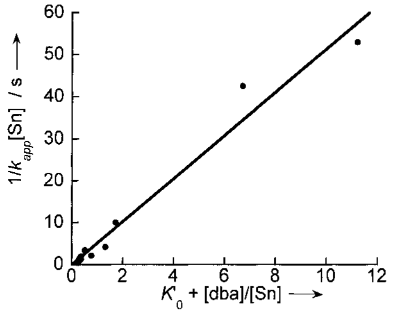

Figure 7. Kinetics of the oxidative addition of PhI (1 mol dm$^{-3}$) to the palladium(0) complex generated from $[Pd^0(dba)_2]$ (1 mmol dm$^{-3}$) and $AsPh_3$ (2 mmol dm$^{-3}$) in the presence of various amounts of $CH_2{=}CH{-}SnBu_3$ in the range 1–10 mmol dm$^{-3}$, and then in the presence of added dba (8 mmol dm$^{-3}$) and for $CH_2{=}CH{-}SnBu_3$ concentrations in the range 1–20 mmol dm$^{-3}$, in DMF at 20 °C monitored by UV spectroscopy. Plot of $1/k_{app}[Sn]$ versus $K'_0$ + [dba]/[Sn] [Eq. (7)].

The effect of the nucleophile, $CH_2{=}CH{-}SnBu_3$, is then to slow down the rate of the oxidative addition. This shows that a nucleophile may interfere in the oxidative addition step before the transmetallation step. This has already been observed with styrene (reagent in Heck reactions), which was found to slow down the oxidative addition of PhI by formation of the unreactive complex $[Pd^0(\eta^2\text{-}CH_2{=}CH\text{-}Ph)(PPh_3)_2]$.[20] In another situation, a major and reactive complex $[Pd^0(\eta^2\text{-}CH_2{=}CH\text{-}CO_2Me)(dppf)]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) was formed when $CH_2{=}CH\text{-}CO_2Me$ was the alkene in a Heck reaction catalyzed by $[Pd^0(dba)_2]$ and dppf.[21]

In a comparison of $PPh_3$ and $AsPh_3$, one sees that the effect of $AsPh_3$ is to increase the rate of the oxidative addition in the absence of $CH_2{=}CH{-}SnBu_3$ in THF and DMF. However, this accelerating effect is partly canceled out in the presence of $CH_2{=}CH{-}SnBu_3$, that is, under the conditions of a true catalytic reaction.

## Conclusion

Relative to $PPh_3$, the effect of $AsPh_3$ when added to $[Pd^0(dba)_2]$ in the ratio 2:1, is to increase the rate of the oxidative addition of PhI by a factor ten in DMF and seven in THF. The reactive species is still a 14-electron complex $[(solv)Pd^0(AsPh_3)_2]$; however, the complex is present at low concentrations because it is involved in an equilibrium with the major but nonreactive complex $[Pd^0(dba)(AsPh_3)_2]$. Once again, dba has a decelerating effect on the rate of the oxidative addition by decreasing the concentration of the reactive species. In contrast to $PPh_3$, the addition of more than two equivalents of $AsPh_3$ to $[Pd^0(dba)_2]$ does not affect the kinetics of the oxidative addition because of the very endergonic displacement of dba from $[Pd^0(dba)(AsPh_3)_2]$ to form $[Pd^0(AsPh_3)_3]$. The higher reactivity observed in the oxidative addition when the ligand is $AsPh_3$ is not caused by thermodynamic factors, since the concentration of the reactive species, $[(solv)Pd^0(AsPh_3)_2]$, is lower than that of $[(solv)Pd^0(PPh_3)_2]$, but rather it is caused by kinetic factors, which make $[(solv)Pd^0(AsPh_3)_2]$ intrinsically more reactive in the oxidative addition elementary step than $[(solv)Pd^0(PPh_3)_2]$. This may only be caused by electronic factors since both ligands have very similar cone angles.

The complex *trans*-$[PhPdI(AsPh_3)_2]$, formed in the oxidative addition, is involved in a slow equilibrium with a T-shaped complex $[PhPdI(solv)(AsPh_3)]$ after appreciable decomplexation of one $AsPh_3$. Yet, up to now, we do not know whether the T-shaped complex contributes or not in the transmetallation step.[1–3]

Under catalytic conditions, that is, in the presence of a nucleophile such as $CH_2{=}CH{-}SnBu_3$, which is able to coordinate $[Pd^0(AsPh_3)_2]$, a new complex is formed, $[Pd^0(\eta^2\text{-}CH_2{=}CH{-}SnBu_3)(AsPh_3)_2]$, which does not react with PhI. $CH_2{=}CH{-}SnBu_3$ makes the oxidative addition slower by decreasing the concentration of the reactive species $[(solv)\text{-}Pd^0(AsPh_3)_2]$. This shows that a nucleophile may be not only involved in the transmetallation step, but may also interfere in the kinetics of the oxidative addition step by modifying the concentration of the reactive species. The accelerating effect of $AsPh_3$ relative to $PPh_3$ is then partially canceled by the decelerating effect of the nucleophile.

As a conclusion of the above study, the mechanism of the oxidative addition in a $[Pd^0(dba)_2]/n AsPh_3$-catalyzed Stille reaction involving PhI and $CH_2{=}CH{-}SnBu_3$ may be described as in Scheme 6. The kinetics of the overall oxidative addition does not depend on the number of equivalents of $AsPh_3$, provided that $n \geq 2$. However, the thermodynamic concentration of the T-shaped complex is dependent on the $AsPh_3$ concentration.

## Experimental Section

$^{31}P$ NMR spectra were recorded on a Bruker spectrometer (101 MHz) with $H_3PO_4$ as an external reference. UV spectra were recorded on a DU 7400 Beckman spectrophotometer. Cyclic voltammetry was performed with a homemade potentiostat and a waveform generator Tacussel GSTP4. The cyclic voltammograms were recorded on a Nicolet 301 oscilloscope.

DMF was distilled from calcium hydride under vacuum and kept under argon. THF was distilled from sodium benzophenone. Triphenylarsine, phenyl iodide, and vinyltributyltin (Aldrich) were commercially available. $[Pd^0(dba)_2]$ was prepared according to a reported procedure.[22]

**Synthesis of *trans*-$[PhPdI(AsPh_3)_2]$**: Anhydrous THF was added to $[Pd(dba)_2]$ (1 g, 1.74 mmol) and $AsPh_3$ (1.065 g, 3.48 mmol) until complete dissolution. PhI (387 µL, 3.48 mmol) was then added. After 2 h, the THF was evaporated. The addition of ethyl ether gave a pale yellow precipitate. Yield: 1.33g (83 %); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.45$ (d, $J = 7$ Hz, 2H;

*o*-H of $AsPh_3$), 7.37 (t, $J = 7$ Hz, 1H; *p*-H of $AsPh_3$), 7.29 (t, $J = 7$ Hz, 2H; *m*-H of $AsPh_3$), 6.72 (d, $J = 7$ Hz, 2H; *o*-H), 6.47 (t, $J = 7$ Hz, 1H; *p*-H), 6.37 (t, $J = 7$ Hz, 2H; *m*-H); the $^1$H NMR spectrum also exhibited the signals of [PhPdI($AsPh_3$)]: $\delta = 7.45$ (d, $J = 7$ Hz, 2H; *o*-H of $AsPh_3$), 7.37 (t, $J = 7$ Hz, 1H; *p*-H of $AsPh_3$), 7.29 (t, $J = 7$ Hz, 2H; *m*-H of $AsPh_3$), 7.13 (d, $J = 7$ Hz, 2H; *o*-H), 6.68 (t, 2H; *m*-H), 6.65 (t, 1H; *p*-H); the single signal of the free $AsPh_3$ at $\delta = 7.37$ overlaps one of the signals of the ligated $AsPh_3$.

**UV experiments**: Mixtures of $[Pd^0(dba)_2]$ (1 mmol dm$^{-3}$) and $AsPh_3$ (2 equiv) in DMF or THF and the suitable amount of PhI or $CH_2{=}CH{-}SnBu_3$ were investigated in a thermostated cell with a 1 mm path length.

**Electrochemical set-up and electrochemical procedure for voltammetry**: Experiments were carried out in a three-electrode cell connected to a Schlenk line. The counter-electrode was a platinum wire of $\approx 1$ cm$^2$ apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge filled with THF or DMF (3 mL) that contained $n$Bu$_4$NBF$_4$ (0.3 mol dm$^{-3}$). THF or DMF (12 mL) containing $n$Bu$_4$NBF$_4$ (0.3 mol dm$^{-3}$) were poured into the cell followed by $[Pd^0(dba)_2]$ (13.8 mg, 0.024 mmol) and $AsPh_3$ (14.7 mg, 0.048 mmol). Cyclic voltammetry was performed at a stationary gold-disk electrode (i.d. 0.5 mm) with a scan rate of 0.5 V s$^{-1}$. The chronoamperometry was performed at a stationary gold-disk electrode (i.d. 0.5 mm) every 50 mV from +1.15 V to +2 V, with duration steps $\theta$ from 0.05–0.5 s. The kinetics of the oxidative addition of PhI was monitored at a rotating gold-disk electrode (i.d. 2 mm) polarized at +0.8 V with an angular velocity of 105 rad s$^{-1}$.

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