Neutral palladium(0) complexes from $Pd(OAc)_2$ and tri-2-furylphosphine and their reactivity in oxidative addition of iodobenzene

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Dedicated to our colleague and dear friend Professor Armand Lattes for the celebration of 50 years of teaching and research

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Abstract

A Pd(0) complex, $S\text{Pd}^0(\text{TFP})_2$ (TFP = tri-2-furylphosphine, *S* = THF, DMF), is spontaneously formed upon addition of 3 equiv TFP to $Pd(OAc)_2$ in THF or DMF. Higher amount of TFP leads to the formation of $\text{Pd}^0(\text{TFP})_3$ in equilibrium with TFP and $S\text{Pd}^0(\text{TFP})_2$. The latter complex is the reactive species in the oxidative addition with PhI leading to *trans*-PhPdI(TFP)_2. The oxidative addition is retarded by excess TFP. Comparison with PPh_3 investigated in a previous work establishes that i) a neutral complex $S\text{Pd}^0(\text{TFP})_2$ is formed rather than the anionic $[\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})]^-$, ii) the rate of formation of $S\text{Pd}^0(\text{TFP})_2$ is faster than that of $[\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})]^-$, iii) $S\text{Pd}^0(\text{TFP})_2$ is more reactive than $[\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})]^-$ in oxidative addition with PhI, iv) the oxidative addition gives the neutral *trans*-PhPdI(TFP) rather than *trans*-$\text{PhPd(OAc)PPh}_3)_2$. $S\text{Pd}^0(\text{TFP})_2$ generated from $Pd(OAc)_2$ and 3 equiv TFP is much more reactive than when it generated from $\text{Pd}^0(\text{dba})_2$ and 2 equiv TFP due to the non interference of $\text{Pd}^0(\text{dba})(\text{TFP})_2$.

Keywords: Palladium, oxidative addition, tri-2-furylphosphine, palladium diacetate

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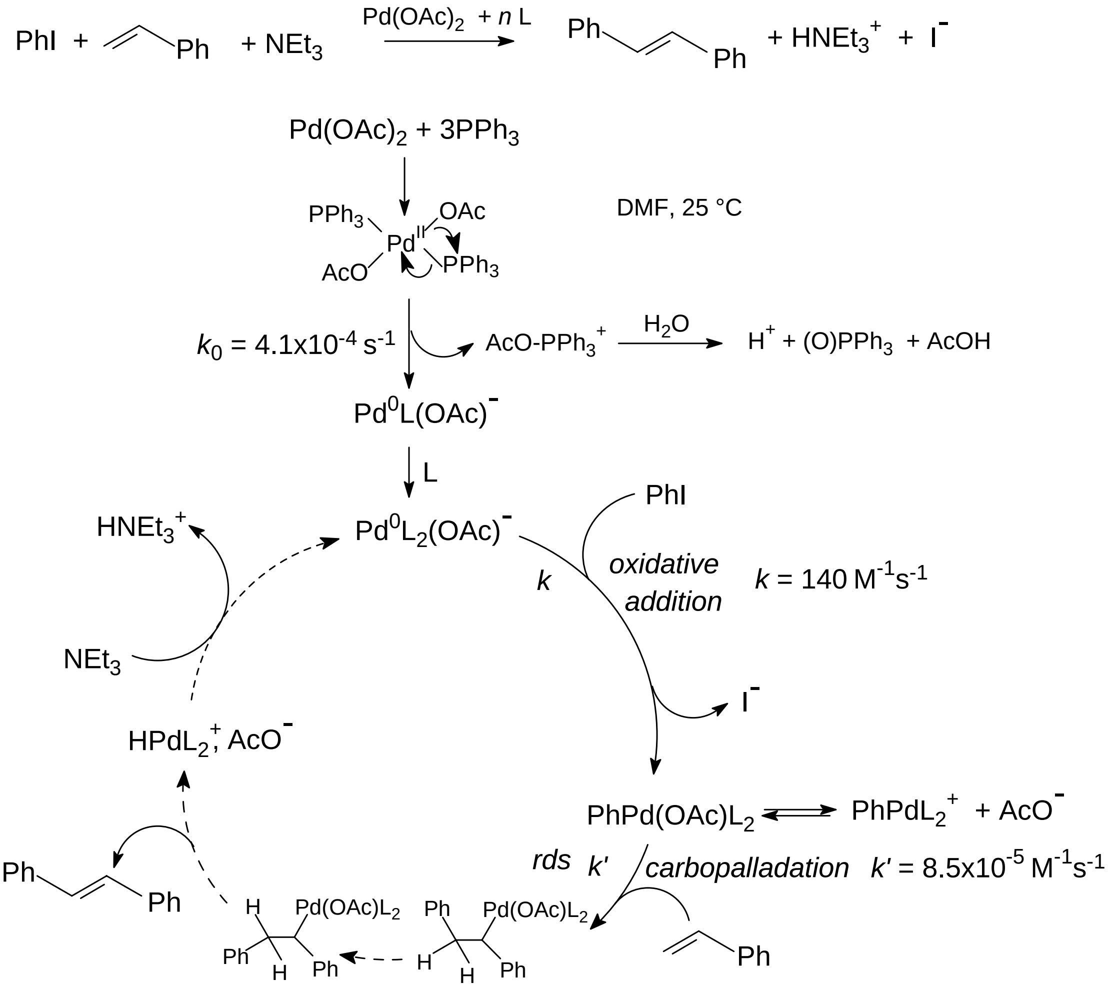
Introduction

We earlier established that Pd(0) complexes were generated in DMF or THF upon mixing $Pd(OAc)_2$ and excess triarylphosphines PR_3 (R = aryl, alkyl),[1] i.e., a set of precursors often used to catalyzed Heck reactions (Scheme 1).[2,3] As far as PPh_3 is concerned, the resulting catalytic palladium(0) species was established to be anionic[3] $[Pd^0(PPh_3)_2(OAc)]^-$ and this structure was further confirmed by DFT calculations (Scheme 1).[4]



Scheme 1

The oxidative addition of $[Pd^0(PPh_3)_2(OAc)]^-$ with iodobenzene gives the unexpected *trans*-$PhPd(OAc)(PPh_3)_2$ which proved to be a key complex involved in the rate determining step of Heck reactions, i.e., in the carbopalladation step with alkenes (Scheme 1).[3] Indeed, *trans*-$PhPd(OAc)(PPh_3)_2$ was found to be much more reactive with the alkene than *trans*-$PhPdI(PPh_3)_2$ which is usually formed in the oxidative addition of PhI with the neutral complex $Pd^0(PPh_3)_2$. The efficient interference of the ions AcO^- delivered by the precursor $Pd(OAc)_2$ in Heck reactions was then clearly established (Scheme 1).[3]

The ligand tri-2-furylphosphine (TFP) has been used by Farina *et al.* in Palladium-catalyzed Stille reactions based upon using $Pd^0(dba)_2$ or $Pd^0{}_2(dba)_3$ as precursors.[5] The structure and reactivity of the ensuing Pd(0) complex in oxidative addition with iodobenzene has been fully investigated in our group leading to the identification of $SPd^0(TFP)_2$ (*S* = THF, DMF) as the reactive complex (Scheme 2).[6] In DMF, such Pd(0) complex was found to be more reactive than the corresponding Pd(0) complexes ligated by PPh_3 when considering overall identical concentrations of the two ligands.[6]

$$Pd^0(dba)_2 + 2\ TFP \longrightarrow Pd^0(dba)(TFP)_2 + dba$$
$$Pd^0(dba)(TFP)_2 \rightleftarrows Pd^0(TFP)_2 + dba$$
$$Pd^0(TFP)_2 + TFP \rightleftarrows Pd^0(TFP)_3$$
$$Pd^0(TFP)_2 + PhI \longrightarrow \textit{trans}\text{-}PhPdI(TFP)_2$$

Scheme 2 (the solvent THF or DMF on low-ligated Pd^0 complexes is voluntarily omitted)

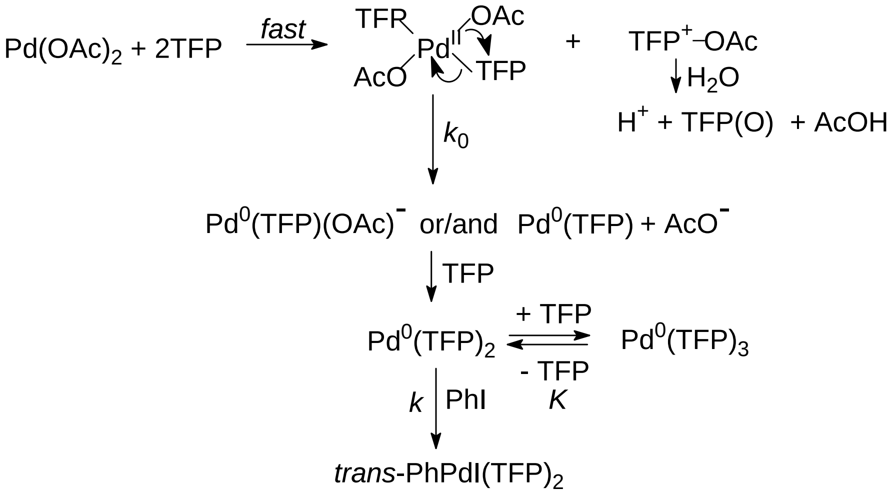
The ligand TFP may also be introduced in Palladium-catalyzed reactions upon using $Pd(OAc)_2$ as the precursor.[7] We report herein that Pd(0) complexes are indeed generated from mixtures of $Pd(OAc)_2$ and tri-2-furylphosphine. In unexpected contrast with the case of PPh_3, upon using TFP, the ensuing Pd(0) complex is no longer anionic and consequently its oxidative addition with PhI does not provide *trans*-$PhPd(OAc)(TFP)_2$ but the classical *trans*-$PhPdI(TFP)_2$.

Results and Discussion

Evidence for the formation of Pd(0) complexes from $Pd(OAc)_2$ and n TFP (n ≥ 3) in THF or DMF

As performed previously for PPh_3,[1,3] the reaction of $Pd(OAc)_2$ with n equiv of TFP ($n \geq 3$) was followed by ^{31}P NMR spectroscopy in THF containing 10 % acetone-d_6 for the lock.[1] After addition of $n = 10$ equivalents of TFP to a solution of $Pd(OAc)_2$ (16 mM) in THF, two main signals were observed: a sharp singlet at $\delta_1 = -14.32$ ppm, assigned to tri-2-furylphosphine oxide TFP(O) by comparison to an authentic sample and a broad signal at $\delta_2 = -66.64$ ppm ($\Delta\nu_{1/2}$ = 460 Hz). The signal of the free TFP at $\delta_0 = -75.63$ ppm was not observed, suggesting that it was involved in an equilibrium with Pd(0) complexes being then responsible for the broad signal at δ_2. After addition of PhI (1 equiv), the broad signal at δ_2 was no longer observed confirming that δ_2 did effectively belong to Pd(0) complexes ligated by TFP. A new sharp singlet appeared at $\delta_3 = -28.22$ ppm. It was assigned to *trans*-$PhPdI(TFP)_2$ by comparison to an authentic sample.[6] The signal of the free TFP at δ_0 was also restored.

The complex $Pd^0(TFP)_3$ generated from $Pd^0(dba)_2$ after addition of excess TFP was characterized in a previous work by ^{31}P NMR as a broad signal at –64.46 ppm in THF, due to the equilibrium between $Pd^0(TFP)_3$, $Pd^0(TFP)_2$ and TFP (third equation in Scheme 2).[6] Consequently, the broad signal at δ_2 characterizes a similar equilibrium. This suggests that $Pd^0(TFP)_3$ undergoes oxidative addition with PhI via $Pd^0(TFP)_2$, as established in Scheme 2 (third and fourth equation). Those Pd(0) complexes have thus been generated in a fast reaction (within less than 20 min, the time required for recording the first ^{31}P NMR spectrum) from the mixture: Pd(OAc)$_2$ + 10 TFP. The primary complex Pd(OAc)$_2$(TFP)$_2$ was not detected by ^{1}P NMR due to its too short life but was characterized in cyclic voltammetry by its reduction peak (E^p = –0.96 V *vs* SCE) recorded 5 min after mixing, just before its fast evolution to Pd(0) complexes (Scheme 3).



Scheme 3 (The solvent THF or DMF on low-ligated Pd^0 complexes is voluntarily omitted)

The complex *trans*-PhPdI(TFP)$_2$ was formed in the oxidative addition and not *trans*-PhPd(OAc)(TFP)$_2$ as expected if anionic [Pd^0(TFP)$_{n'}$(OAc)]$^-$ (n' = 2, 3) had been formed and involved in the oxidative addition. Moreover, I$^-$ ions were not released during the oxidative addition step, as it occurred for the oxidative addition of [Pd^0(PPh$_3$)$_2$(OAc)]$^-$ (Scheme 1).[3] This suggests that complexes Pd^0(TFP)$_{n'}$ (n' = 2, 3) generated from Pd(OAc)$_2$(TFP)$_2$ are neutral and not coordinated by the acetate ion (Scheme 3). It is only upon addition of large excess AcO$^-$ (10 equiv nBu$_4$NOAc) that *trans*-PhPdI(TFP)$_2$ partially disappeared in THF to afford a new complex characterized by a singlet at δ_4 = –23.64 ppm and assigned to *trans*-PhPd(OAc)(TFP)$_2$ formed in 34 % yield (Scheme 4). The same complex *trans*-PhPd(OAc)(TFP)$_2$ was formed upon addition of AcO$^-$ (10 equiv.) to the isolated *trans*-PhPdI(TFP)$_2$ complex generated through the sequence of reactions in Scheme 2. This shows that the equilibrium of Scheme 4 lies in favor of *trans*-PhPdI(TFP)$_2$ for low ratio [AcO$^-$]/[*trans*-PhPdI(TFP)$_2$].

$$\textit{trans}\text{-PhPdI(TFP)}_2 + \text{AcO}^- \rightleftharpoons \textit{trans}\text{-PhPd(OAc)(TFP)}_2 + \text{I}^-$$

Scheme 4

The formation of a Pd(0) complex from Pd(OAc)$_2$ and 4 TFP in DMF was followed by cyclic voltammetry. This allows the characterization and titration of Pd(II) or Pd(0) complexes at times shorter than those required to obtain a first ^{31}P NMR spectrum. A yellow solution is formed after addition of TFP (8 mM) to a brown solution of $Pd(OAc)_2$ (2 mM) in DMF containing $n\mathrm{Bu_4NBF_4}$ (0.3 M). An irreversible reduction peak at $E^{p}_{R1} = -0.12$ V *vs* SCE is then observed in the first recorded CV (2 min after mixing) assigned to $Pd(OAc)_2(TFP)_2$. This reduction peak disappeared with time and an irreversible oxidation peak was then observed at $E^{p}_{O1} = +0.36$ V vs SCE when the CV was performed directly to oxidation, attesting to the formation of a Pd(0) complex from $Pd(OAc)_2(TFP)_2$. Accordingly, this oxidation peak current increased with time (Fig 1a) but was no longer observed after addition of PhI (2 mM). In a previous work, the $Pd^0(TFP)_3$ complex generated together with $Pd^0(dba)(TFP)_2$ after addition of TFP (8 mM) to $Pd^0(dba)_2$ (2 mM) in DMF (Scheme 2) had been characterized by an oxidation peak at +0.36 V,[6] thus identical to the oxidation peak potential of the Pd(0) observed above, generated from $Pd(OAc)_2$ + 4 TFP.

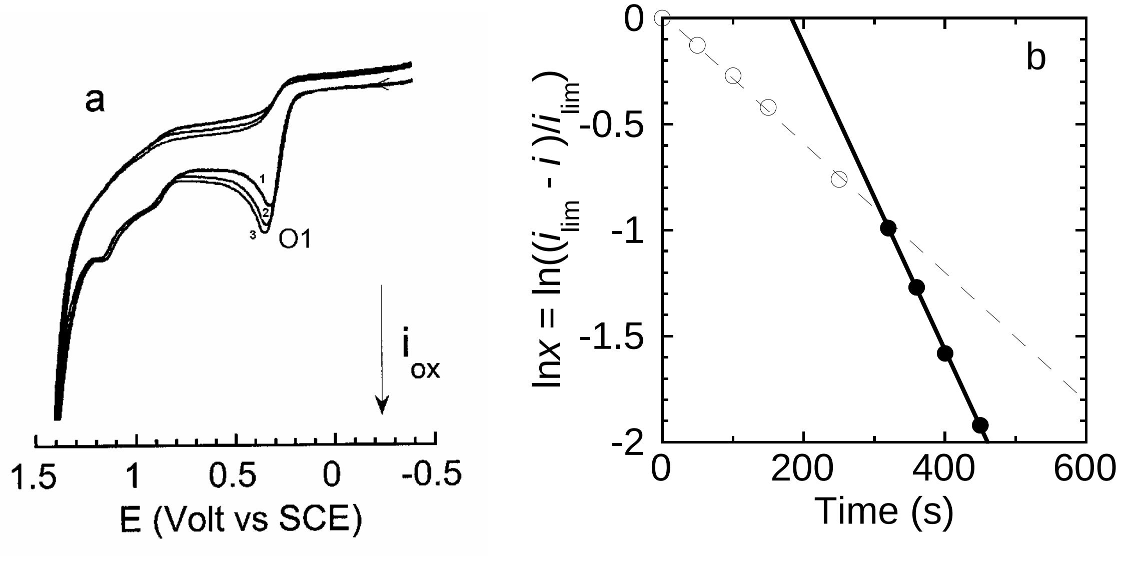


Figure 1. a) Cyclic voltammetry of $Pd^0(TFP)_3$ generated from $Pd(OAc)_2$ (2 mM) and 4 equiv TFP in DMF containing $n\mathrm{Bu_4NBF_4}$ (0.3 M) versus time. **1**: 5 min; **2**: 23 min; **3**: 26 min. Steady gold disk electrode (d 0.5 mm), scan rate: 0.2 $\mathrm{Vs^{-1}}$. b) Kinetics of the formation of $Pd^0(TFP)_3$ generated from $Pd(OAc)_2$ (2 mM) and 10 equiv TFP in DMF containing $n\mathrm{Bu_4NBF_4}$ (0.3 M). Plot of ln$x$ ($x = (i_{\mathrm{lim}} - i_t)/i_{\mathrm{lim}}$) against time.

The rate of formation of the Pd(0) complex from $Pd(OAc)_2$ + 10 TFP was determined in DMF by amperometry at a rotating disk electrode polarized at +0.4 V, on the plateau of the oxidation wave of the Pd(0) complex, as done in the case of PPh_3.[1] The increase of the oxidation plateau current (proportional to the Pd(0) concentration) was recorded with time until a limiting value was observed, attesting to the end of the reaction. The plot of ln$x$ ($x = (i_{\mathrm{lim}} - i_t)/i_{\mathrm{lim}}$; i_{lim}: final oxidation current; i_t: oxidation current at t) against time gave two straight lines (Fig 1b) as in the case of PPh_3,[1] due to the formation of an intermediate low-ligated Pd(0) complex before its final stabilization by an extra ligand leading to $Pd^0(TFP)_3$ (Scheme 3).[8] The rate constant k_0 (Scheme 3) for the formation of the Pd(0) complex was determined from the slope of the straight line obtained at longest times:

$$k_0 = 7.2\times10^{-3}\ s^{-1}\ (DMF\ 25\ °C).$$

All these results confirm that the reactions proposed in Scheme 3 take place in DMF and THF. A Pd^0 complex is generated from $Pd(OAc)_2(TFP)_2$ in a fast reaction.

Kinetics and mechanism of the oxidative addition of PhI to the Pd(0) complexes generated from $Pd(OAc)_2$ and n TFP ($n \geq 3$) in THF or DMF

When 1 equiv PhI was added to the $Pd^0(TFP)_2$ generated from $Pd(OAc)_2$ (C_0 = 2 mM) associated to 3 equiv TFP in DMF containing nBu_4NBF_4 (0.3 M), the oxidation plateau current of $Pd^0(TFP)_2$ (proportional to its concentration) decreased due to the oxidative addition process (Scheme 5). The kinetics of the oxidative addition was then followed by amperometry at a rotating disk electrode polarized at +0.4 V on the plateau of the oxidation wave of $Pd^0(TFP)_2$, by recording the decrease of the oxidation plateau current until total conversion.

$$Pd(OAc)_2 + 3TFP + H_2O \xrightarrow{k_0} Pd^0(TFP)_2 + AcO^- + H^+ + TFP(O) + AcOH$$

$$Pd^0(TFP)_2 + PhI \xrightarrow{k} \textit{trans}\text{-}PhPdI(TFP)_2$$

Scheme 5

Under stoichiometric conditions, the kinetic law is given in Eq 1 ($x = [Pd^0]_t/[Pd^0]_0 = i_t/i_0$; i_t: oxidation current of $Pd^0(TFP)_2$ at t, i_0: initial oxidation current).

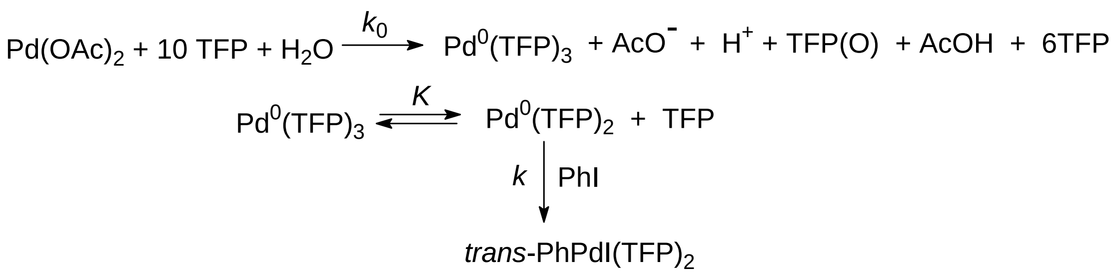
$$1/x = kC_0t + 1 \qquad (1)$$

The plot of $1/x$ against time was linear (Fig 2a) establishing a first order reaction for $Pd^0(TFP)_2$ and PhI. The rate constant k was determined from the slope of the straight line according to Eq 1.

$$k = 99\ (\pm2)\ M^{-1}s^{-1}\ (DMF,\ 25\ °C)$$

The effect of acetate ions was tested by adding 10 equiv AcO^- to the Pd(0) generated from $Pd(OAc)_2$ + 3 TFP before introduction of PhI. From the value of $t_{1/2}$ given in Table 1, one deduce that the kinetics was not significantly affected by the added acetate ions, establishing definitively that $Pd^0(TFP)_2$ generated from $Pd(OAc)_2$ associated with 3 equiv TFP did not equilibrate significantly with acetate ions in DMF.

A similar experiment was performed starting from $Pd^0(TFP)_3$ generated from $Pd(OAc)_2$ (C_0 = 2 mM) and 10 equiv TFP in DMF. From the half reaction $t_{1/2}$ given in Table 1, one notes that the oxidative addition of PhI was slower due to the excess of ligand (6 free equivalents after reaction) and the formation of the unreactive $Pd^0(TFP)_3$ (Scheme 6). The kinetic law is given in Eq 2.



Scheme 6

$$1/x = kKC_0t/[\mathrm{TFP}] + 1 \qquad (2)$$

$kK = 0.01\ \mathrm{s}^{-1}$ was determined from the slope of the straight line obtained by plotting $1/x$ against time (Fig 2b).[9] Since $k = 99\ \mathrm{M}^{-1}\mathrm{s}^{-1}$ is known (vide supra), the equilibrium constant $K = ([\mathrm{Pd}^0(\mathrm{TFP})_2][\mathrm{TFP}]/[\mathrm{Pd}^0(\mathrm{TFP})_3])_{\mathrm{equil}}$ could be determined.

$$K = 1\times10^{-4}\ \mathrm{M}\ (\mathrm{DMF}, 25\ °\mathrm{C})$$

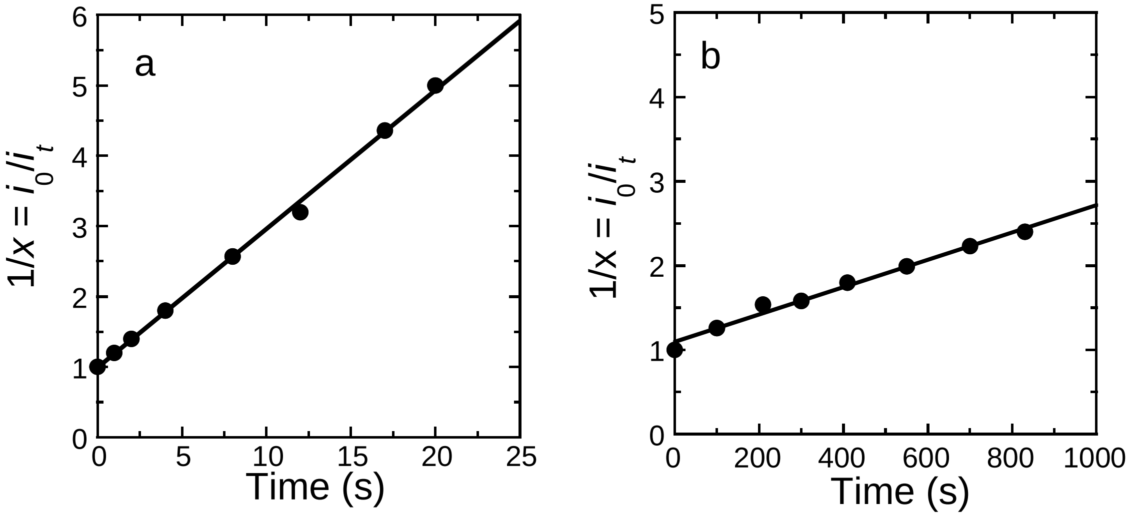


Figure 2. Kinetics of the oxidative addition of PhI (2 mM) with $\mathrm{Pd}^0(\mathrm{TFP})_2$ generated from $\mathrm{Pd(OAc)_2}$ (2 mM) and *n* equiv TFP in DMF containing $n\mathrm{Bu_4NBF_4}$ (0.3 M) at 25 °C. Plot of $1/x$ against time: a) $n = 3$; b) $n = 10$.

Similar procedure was used to follow the kinetics of the oxidative addition in THF (Table 1). Under similar concentrations, the oxidative addition performed from $\mathrm{Pd}^0(\mathrm{TFP})_2$ generated from $\mathrm{Pd(OAc)_2}$ ($C_0 = 2$ mM) associated with 3 equiv TFP was found to be faster in THF than in DMF leading to less accurate data for the determination of *k* (Table 1). This suggests a coordination of $\mathrm{Pd}^0(\mathrm{TFP})_2$ by DMF since this is expected to be stronger than by THF. In THF, the oxidative addition proceeded also slower in presence of excess TFP (n = 10) (Table 1) as in DMF, due to the formation of the non reactive $Pd^0(TFP)_3$.[6]

Table 1. Kinetic and thermodynamic data for the oxidative addition of PhI (2 mM) with $Pd^0(TFP)_2$ generated from $Pd(OAc)_2$ (2 mM) and n TFP (n = 3 or 10) in THF or DMF. See Schemes 5 and 6 for the definition of k and K

Precursor of Pd^0	$t_{1/2}$ (s)		k ($M^{-1}s^{-1}$)		kK (s^{-1})		K (M)	
	DMF	THF	DMF	THF	DMF	THF	DMF	THF
$Pd(OAc)_2$ + 3 TFP	5.1	~1	99±2	500±200	-	-	-	-
$Pd(OAc)_2$ + 10 TFP	556	190	-	-	0.01	0.035	1×10^{-4}	n.d.
$Pd(OAc)_2$ + 3 TFP + 10 AcO^-	4.6	n.d.	-	-	-	-	-	-

It is worthwhile to note that the kinetics of the oxidative addition of PhI (1 equiv) with the Pd(0) complexes generated from $Pd(OAc)_2$ (2 mM) and TFP (6 mM) in THF or DMF was not affected when performed in the presence of NEt_3 (6 mM). This contrasts with the decelerating effect of NEt_3 observed for the anionic $[Pd^0(PPh_3)_2(OAc)]^-$ generated from $Pd(OAc)_2$ (2 mM) and PPh_3 (6 mM).[3] This effect was rationalized as a stabilization of $[Pd^0(PPh_3)_2(OAc)]^-$ vis à vis its decomposition to the more reactive $Pd^0(PPh_3)_2$ and OAc^-, which is a consequence of the interaction of OAc^- with H^+ generated together with $[Pd^0(PPh_3)_2(OAc)]^-$ (Scheme 1).[3] The non effect of NEt_3 in the case of the TFP ligand is henceforth an indirect proof that the Pd(0) complex generated from $Pd(OAc)_2$ and TFP is definitively not ligated by an acetate ion but is neutral: $SPd^0(TFP)_2$ (S = THF or DMF), as well as our former rationalization of the role of NEt_3 in the PPh_3 case.[3]

Conclusion: Comparison TFP/PPh_3

A palladium(0) complex is generated upon addition of TFP or PPh_3 to $Pd(OAc)_2$ by an intramolecular reduction of the Pd(II) center by the ligand in $Pd(OAc)_2(TFP)_2$ or $Pd(OAc)_2(PPh_3)_2$ respectively with formation of the corresponding phosphine oxide. The formation of the Pd(0) complex from $Pd(OAc)_2$ associated to n equiv TFP ($n \geq 3$) is faster ($k_0 = 7.2\times10^{-3}\ s^{-1}$) than that that involving PPh_3 ($k_0 = 4.1\times10^{-4}\ s^{-1}$)[1,3] in DMF at 25 °C. From the relative position of the reduction peaks potential of $Pd(OAc)_2(TFP)_2$ (–0.12 V) and $Pd(OAc)_2(PPh_3)_2$ (–1.23 V) determined in DMF,[1] one observes that TFP is prone to be less electron rich than PPh_3.[10] Accordingly, the intramolecular reduction proceeding via the attack of the acetate onto the ligand L of $Pd(OAc)_2L_2$ (Schemes 1 and 3) should be indeed easier for TFP than for PPh_3, as observed experimentally.

The structure of the resulting Pd(0) complex generated from $Pd(OAc)_2$ + 3 equiv L differs: formation of neutral complexes $S\mathrm{Pd}^0(\mathrm{TFP})_2$ (S = THF or DMF) in contrast to the anionic complex $[Pd^0(PPh_3)_2(OAc)]^-$.[3] In DMF at 25 °C, at identical PhI concentration and in presence of NEt_3, $S\mathrm{Pd}^0(\mathrm{TFP})_2$ was found to be more reactive than $[Pd^0(PPh_3)_2(OAc)]^-$ [3] (k = 99 $M^{-1}s^{-1}$ and 65 $M^{-1}s^{-1}$ respectively). However, in absence of NEt_3, due to the partial involvement of $Pd^0(PPh_3)_2$ from $[Pd^0(PPh_3)_2(OAc)]^-$,[3] $S\mathrm{Pd}^0(\mathrm{TFP})_2$ was found to be less reactive (k = 140 $M^{-1}s^{-1}$ and 99 $M^{-1}s^{-1}$ respectively), which can be rationalized again by the fact that TFP is a less electron-rich ligand than PPh_3. Complexes *trans*-$PhPd(OAc)(PPh_3)_2$ [3] and *trans*-$PhPdI(TFP)_2$ are formed in the oxidative addition of PhI with the Pd(0) complexes generated from $Pd(OAc)_2$ associated with PPh_3 and TFP respectively. *trans*-$PhPd(OAc)(TFP)_2$ is only formed in presence of acetate ions with may be introduced as a base in Heck reactions

At identical concentrations of the precursors and PhI, the complex $S\mathrm{Pd}^0(\mathrm{TFP})_2$ generated from $Pd(OAc)_2$ + 3 TFP is much more reactive than when it generated from $Pd^0(dba)_2$ + 2 TFP in THF or DMF, due to the involvement of the unreactive $Pd^0(dba)(TFP)_2$ in the overall mechanism in the latter case.[6] These results stress once more time the important role of the precursor of the Pd(0) active in catalytic cycles. Indeed the precursor controls the structure and reactivity of the Pd(0) in oxidative additions as well as the structure and reactivity of the aryl-palladium(II) complexes formed in the oxidative addition.

Experimental Section

General Procedures. ^{31}P NMR spectra were recorded on a Bruker spectrometer (101 MHz) in DMF or THF containing 10% of acetone-d_6. Cyclic voltammetry was performed with a home made potentiostat and a wave form generator Radiometer-Tacussel GSTP4. The cyclic voltammograms were recorded on a Nicolet 301 oscilloscope.

Chemicals. DMF was distilled from calcium hydride under vacuum and kept under argon. THF was distilled from sodium-benzophenone. $Pd(OAc)_2$, PhI, $n\mathrm{Bu}_4\mathrm{NOAc}$, $n\mathrm{Bu}_4\mathrm{NBF}_4$, tri-2-furylphosphine, NEt_3 were commercial. *Trans*-PhPdI(TFP) was synthesized according to literature.[6]

Electrochemical set-up and electrochemical procedure for voltammetry. Experiments were carried out in a three-electrode thermostated cell (25 °C) connected to a Schlenk line. The reference was a saturated calomel electrode (Radiometer) separated from the solution by a bridge filled with 3 mL of DMF containing $n\mathrm{Bu}_4\mathrm{NBF}_4$ (0.3 M). The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area. 15 mL of DMF or THF containing n-$\mathrm{Bu}_4\mathrm{NBF}_4$ (0.3 M) were introduced into the cell followed by 21 mg (0.09 mmol) of TFP and 6.7 mg (0.03 mmol) of

$Pd(OAc)_2$. Cyclic voltammetry was performed at a steady gold disk electrode (d 0.5 mm) at a scan rate of 0.2 Vs^{-1}. In other experiments the amount of TFP was increased to 4 or 10 equiv.

Electrochemical procedure for the kinetics of formation of the Pd(0) complex and its reactivity in oxidative addition with PhI

15 mL of DMF containing $n\mathrm{Bu}_4\mathrm{NBF}_4$ (0.3 M) were introduced into the cell followed by 69 mg (0.3 mmol) of TFP and 6.7 mg (0.03 mmol) of $Pd(OAc)_2$ at 25 °C The kinetic measurements for the Pd^0 formation were performed at a rotating gold disk electrode (d 2 mm, $\omega = 105$ rad s^{-1}) polarized at +0.4 *vs* SCE. The increase of the oxidation current of $Pd^0(TFP)_3$ was recorded until a limiting current was observed ($i_{\lim}$ in text).

Once the Pd(0) was formed, 3.4 µL (0.03 mmol) of PhI were added and the kinetics of the oxidative addition was investigated using the same technique. The decrease of the oxidation current was recorded until total conversion. Other experiments were similarly performed in the presence of 12.5 µL (0.09 mmol) of NEt_3 or 90 mg (0.3 mmol) $n\mathrm{Bu}_4\mathrm{NOAc}$ added before PhI.

Acknowledgements

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8. See Ref 1(2) for the kinetic law.
9. Since the free TFP concentration varied from $6C_0$ to $7C_0$ during the oxidative addition, an average value of $6.5C_0$ was used in Eq 2.
10. From previous work, it has been established that the oxidation potential of (DMF)Pd^0(TFP)$_2$ (0.34 V) is more positive than that of (DMF)Pd^0(PPh$_3$)$_2$ (0.14 V)[6] which shows that TFP is less electron rich than PPh$_3$. Note that we are not comparing E^0 but E^P potentials, so kinetic effects are also involved and not only pure thermodynamics.