Comparative Reactivity of Palladium(0) Complexes Generated in Situ in Mixtures of Triphenylphosphine or Tri-2-furylphosphine and Pd(dba)$_2$

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For PPh$_3$, mixtures of Pd(dba)$_2$ and nTFP (TFP = tri-2-furylphosphine, $n \geq 2$) in DMF and THF (S) lead to the formation of Pd(dba)(TFP)$_2$, SPd(TFP)$_3$ in equilibrium with SPd(TFP)$_2$. The substitution of dba by the phosphine in Pd(dba)L$_2$ to form SPdL$_3$ is easier for L = TPF than for L = PPh$_3$. The less ligated complex SPd(TFP)$_2$ is the reactive species in the oxidative addition with phenyl iodide. In THF, {Pd(dba)$_2$ + nTFP}, a mixture often used as a catalyst promoter in several synthetic organic reactions, is found to be less reactive than {Pd(dba)$_2$ + nPPh$_3$} for small values of n (n = 2 or 4) whereas it is more reactive for higher values of n ($n > 6$). Conversely, in DMF, {Pd(dba)$_2$ + nTFP} is always found to be more reactive than {Pd(dba)$_2$ + nPPh$_3$} whatever n ($n \geq 2$).

Introduction

Among the various precursors of palladium(0) complexes, mixtures of Pd(0)(dba)$_2$ (dba = *trans,trans*-dibenzylidenacetone) and phosphine ligands afford efficient palladium(0) catalysts.[1−5] We have previously reported a mechanistic investigation concerning the effective palladium(0) catalytic species generated in situ in a mixture of Pd(dba)$_2$ with triphenylphosphine,[2] para-substituted triphenylphosphines,[5] and bidentate phosphine ligands.[4] As a result, it has been shown that dba is not a labile ligand, since a stable complex Pd(dba)L$_2$ is always formed as the major complex. This complex is involved in an equilibrium with a less ligated complex PdL$_2$, which is the more reactive species in the oxidative addition with aryl halide. In DMF and THF (noted S hereafter), the following mechanism has been established for monodentate ligands L such as triarylphosphines (Scheme 1).[2,5]

Scheme 1

$$\mathrm{Pd(0)(dba)_2} + 2\mathrm{L} \rightarrow \mathrm{Pd(0)(dba)L_2} + \mathrm{dba} \qquad (1)$$

$$\mathrm{Pd(0)(dba)L_2} + S \leftrightarrows S\mathrm{Pd(0)L_2} + \mathrm{dba} \qquad K_1 = \frac{[S\mathrm{PdL_2}][\mathrm{dba}]}{[\mathrm{Pd(dba)L_2}]} \qquad (2)$$

$$\mathrm{Pd(0)(dba)L_2} + \mathrm{L} \leftrightarrows S\mathrm{Pd(0)L_3} + \mathrm{dba} \qquad K_0 = \frac{[S\mathrm{PdL_3}][\mathrm{dba}]}{[\mathrm{Pd(dba)L_2}][\mathrm{L}]} \qquad (3)$$

$$S\mathrm{Pd(0)L_3} \leftrightarrows S\mathrm{Pd(0)L_2} + \mathrm{L} \qquad K_2 = \frac{[S\mathrm{PdL_2}][\mathrm{L}]}{[S\mathrm{PdL_3}]} = K_1/K_0 \qquad (4)$$

$$S\mathrm{Pd(0)L_2} + \mathrm{ArX} \rightarrow \mathrm{ArPdXL_2} + S \qquad \mathrm{k} \qquad (5)$$

As previously established,[2,5] the *overall reactivity* of {Pd(dba)$_2$ + nL} in the oxidative addition with an aryl halide depends (i) on the value of the intrinsic rate constant k of the *elementary step* of the oxidative addition of the reactive species SPd(0)L$_2$ (eq 5) (more basic the phosphine, higher k) and (ii) on the concentration of the active species itself, viz. SPd(0)L$_2$. This concentration is controlled by the values of the two equilibrium constants K_1 and K_0 (eqs 2−4). Since the three species SPd(0)L$_3$, Pd(0)(dba)L$_2$, and SPd(0)L$_2$ are interconnected by three equilibria (eqs 2−4), only two equilibrium constants such as K_1 and K_0 are required

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(1) For the use of Pd(dba)$_2$ with bidentate ligands, see ref 10 in ref 2 of this paper.

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(5) Amatore, C.; Jutand, A.; Meyer, G. *Inorg. Chim. Acta* **1998**, *273*, 76.

(6) For the use of Pd(dba)$_2$ + nTPF, see: (a) Farina, V.; Baker, S. R.; Begnini, D.; Sapino, C., Jr. *Tetrahedron Lett.* **1988**, *29*, 5739. (b) Farina, V.; Baker, S. R.; Sapino, C., Jr. *Tetrahedron Lett.* **1988**, *29*, 6043. (c) Obora, Y.; Tsuji, Y.; Kobayashi, M.; Kawamura, T. *J. Org. Chem.* **1995**, *60*, 4647. (d) Traumer, F.; Le Floch, P.; Lefour, J. M.; Ricard, L.; Mathey, F. *Synthesis* **1995**, 717. (e) Castro, J.; Balme, G.; Gore, J. *J. Chem. Res.* **1995**, *12*, 504. (f) Moreno-Manas, M.; Perez, M.; Pleixats, R. *J. Org. Chem.* **1996**, *61*, 2346. (g) Rottaelander, M.; Palmer, N.; Knochel, P. *Synlett* **1996**, *6*, 573. (h) Stevenson, T. M.; Prasad, A. S. B.; Citineni, J. R.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 8375. (i) Tamao, K.; Ohno, S.; Yamagushi, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1873.

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Table 1. ^{31}P NMR Chemical Shifts[a] of the Palladium(0) Complex Generated in Situ in Mixtures of $Pd(dba)_2$ and 2TFP

		$Pd(0)(dba)(TFP)_2$		
solvent	TFP δ_0	δ_1	δ_2	$PhPdI(TFP)_2$ δ_3
DMF	−76.19	−36.26	−33.71	−28.36
THF	−75.24	−36.54	−33.84	−27.83

[a] ^{31}P NMR chemical shifts of the complex $PhPdI(TFP)_2$ resulting from the oxidative addition with PhI. In ppm vs H_3PO_4 as an external reference.

to express the concentration of $SPd(0)L_2$ comparatively to that of $SPd(0)L_3$ and $Pd(0)(dba)L_2$. Depending on the basic properties of the phosphines, evolution of the concentration and of the intrinsic reactivity of $SPdL_2$ (k in eq 5) could be antagonist, leading to nonlinear correlation of the reactivity with the basicity of the phosphine, as established for para-substituted triphenylphosphines.[5]

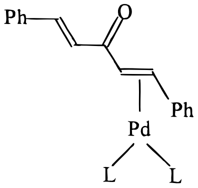
Catalytic reactions involve successive elemental steps (oxidative addition, ligand exchange, reductive elimination, etc.) whose respective rates depend on the nature of the ligand with, as a consequence, a possible inversion of the rate-determining step. In palladium(0)-catalyzed reactions involving aryl halides, it is generally admitted that the first step of the catalytic cycle is oxidative addition of a palladium(0) complex with the aryl halide. It is, therefore, of interest to compare the reactivity of the oxidative addition of the palladium(0) complexes generated in situ in mixtures of $Pd(dba)_2$ with phosphines ligands as a function of the ligand. In 1988, a new ligand tri-2-furylphosphine (TFP) was tested by Farina[6a] in reactions catalyzed by mixtures of $Pd(dba)_2$[6] or $Pd_2(dba)_3$[7] and phosphine ligands. More efficient catalytic systems were very often observed when switching from triphenylphosphine to tri-2-furylphosphine.[6,7] We wish, therefore, to report our investigation on the comparative reactivity of $\{Pd(dba)_2 + n\text{TFP}\}$ with that of $\{Pd(dba)_2 + nPPh_3\}$[2] in oxidative addition with phenyl iodide. In DMF, $\{Pd(dba)_2 + n\text{TFP}\}$ is always more reactive than $\{Pd(dba)_2 + nPPh_3\}$ whatever n ($n \geq 2$). In THF, $\{Pd(dba)_2 + n\text{TFP}\}$ is more reactive than $\{Pd(dba)_2 + nPPh_3\}$ when $n > 6$ whereas it is less reactive when $n < 6$. This may have important consequences on the kinetics of the overall catalytic reaction.

Results and Discussion

Identification of the Palladium(0) Complexes Formed in Situ in a Mixture of $Pd(dba)_2 + n$TFP ($n \geq 2$) in DMF and THF as Investigated by ^{31}P NMR Spectroscopy. In DMF, a set of 2 broad signals δ_1 and δ_2 of equal magnitude were observed in the ^{31}P NMR spectrum of a mixture of $Pd(dba)_2$ + 2TFP while the signal δ_0 of the free ligand was not detected (Table 1), eq 6. As already established for PPh_3,[2,8] the presence

$$Pd(0)(dba)_2 + 2\text{TFP} \rightarrow Pd(0)(dba)(\text{TFP})_2 + \text{dba} \quad (6)$$

of two different phosphorus atoms is due to a monoligation of the ligand dba in the complex $Pd(dba)(TFP)_2$. However, the signals were too broad ($\Delta\nu_{1/2}$ = 85 Hz) to allow determination of the coupling constant J_{PP}. In



the presence of 10 equiv of phenyl iodide, a new signal at δ_3 appeared instead of δ_1 and δ_2 (Table 1). This signal characterizes the trans complex $PhPdI(TPF)_2$ formed in the oxidative addition (eq 7).[9]

$$Pd(0)(dba)(\text{TFP})_2 + \text{PhI} \rightarrow \text{PhPdI}(\text{TPF})_2 + \text{dba} \quad (7)$$

In the mixtures of $Pd(dba)_2 + n$TFP ($n > 4$), the two signals at δ_1 and δ_2 disappeared and a broad signal was detected at δ_4 (e.g., $n = 8$, $\delta_4 = -64.46$ ppm, $\Delta\nu_{1/2}$ = 202 Hz). Despite the excess of ligand, the signal of the free phosphine at δ_0 was never observed. This means that addition of more than 2 equiv of TFP to $Pd(dba)_2$ affords a palladium(0) complex involved in an equilibrium with the ligand (eqs 8 and 9). In the presence of

$$Pd(0)(dba)(\text{TFP})_2 + \text{TFP} \leftrightarrows SPd(0)(\text{TFP})_3 + \text{dba} \qquad K_0^{\text{TFP}} \quad (8)$$

$$SPd(0)(\text{TPF})_3 \leftrightarrows SPd(0)(\text{TPF})_2 + \text{TFP} \qquad K_2^{\text{TFP}} \quad (9)$$

phenyl iodide, the signals δ_3 of $PhPdI(TFP)_2$ and δ_0 of the free ligand were detected. We noticed that in mixtures of $Pd(dba)_2$ + 4TFP, the two signals of $Pd(dba)(TFP)_2$ were no longer observed, but surprisingly, no other signals could be detected in the ^{31}P NMR spectrum. However, after addition of 10 equiv of PhI into the NMR tube, the signals δ_3 of $PhPdI(TFP)_2$ and δ_0 of free TFP were observed, suggesting that the signal of the palladium(0) formed from $Pd(dba)_2$ + 4TFP was so broad that it could not be detected.

The same investigation was undertaken in THF (Table 1) but will not be discussed here since the ^{31}P NMR spectra were very similar to those reported by Farina for mixtures of $Pd_2(dba)_3$ and 4TFP.[7b]

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(7) For the use of $Pd_2(dba)_3 + n$TPF, see: (a) Farina, V.; Hauck, S. I. *Synlett* **1991**, *3*, 157. (b) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. (c) Farina, V.; Firestone, R. A. *Tetrahedron* **1993**, *49*, 803. (d) Farina, V.; Krishna, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434. (e) Siesel, D. A.; Staley, S. W. *Tetrahedron Lett.* **1993**, *34*, 3679. (f) Siesel, D. A.; Staley, S. W. *J. Org. Chem.* **1993**, *58*, 7870. (g) Badone, D.; Cardamone, R.; Guzzi, U. *Tetrahedron Lett.* **1994**, *35*, 5477. (h) Busacca, C. A.; Swestock, J.; Johnson, R. E.; Bailey, T. R.; Musza, L.; Rodger, C. A. *J. Org. Chem.* **1994**, *59*, 7553. (i) Yang, Y.; Wong, H. N. C. *Tetrahedron Lett.* **1994**, *50*, 9583. (j) Casson, S.; Kocienski, P.; Reid, G.; Smith, N.; Street, J. M.; Webster, M. *Synthesis* **1994**, 1301. (k) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266. (l) Caldirola, P.; Chowdury, R.; Johansson, A. M.; Hacksell, U. *Organometallics* **1995**, *14*, 3897. (m) Koo, S.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1995**, *117*, 3389. (n) Goux, C.; Massacret, M.; Lhoste, P.; Sinou, D. *Organometallics* **1995**, *14*, 4585. (o) Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426. (p) Attwood, M. R.; Raynham, T. M.; Smyth, D. G.; Stephenson, G. R. *Tetrahedron Lett.* **1996**, *37*, 2731. (q) Wolfe, J. P.; Rennels, R. A.; Buchwald, S. L. *Tetrahedron* **1996**, *52*, 7525. (r) Fournier-Nguefack, C.; Lhoste, P.; Sinou, D. *Tetrahedron* **1997**, *53*, 4353.

(8) Herrmann, W. A.; Thiel, W. R.; Brossmer, C.; Öfele, K.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, *461*, 51.

(9) (a) The complex $PhPdI(TPF)_2$ was also slowly formed by addition of 2 equiv of TFP to a solution of $PhPdI(PPh_3)_2$ according to the reaction: $PhPdI(PPh_3)_2 + 2\text{TFP} \rightarrow PhPdI(TPF)_2 + 2PPh_3$ (eq I). (b) Substitution of TFP by PPh_3 in $PhPdI(TPF)_2$ to form $PhPdI(PPh_3)_2$ is faster than in eq I,[9a] suggesting that PPh_3 is a better ligand than TPF for palladium(II), i.e., PPh_3 is more basic than TFP.[7b]

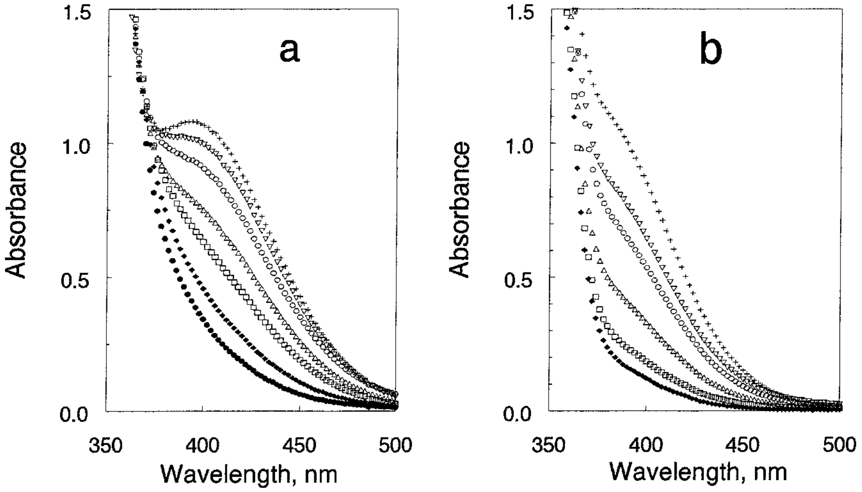


Figure 1. UV spectrum performed in DMF in a 1 mm path length cell at 20 °C. (a) $Pd(dba)_2$ (0.1 mmol dm^{-3}) + n equiv of PPh_3: $n = 2$ (+), 4 (▽), 6 (○), 10 (△), 20 (□), 50 (◆), 100 (●). (b) $Pd(dba)_2$ (1 mmol dm^{-3}) + n equiv of TFP: $n = 2$ (+), 4 (▽), 6 (○), 10 (△), 20 (□), 50 (◆).

Identification of the Palladium(0) Complexes Formed in Situ in a Mixture of $Pd(dba)_2$ + nTFP ($n \geq 2$) in DMF as Investigated by UV Spectroscopy. As already reported,[5] the complex $Pd(dba)(PPh_3)_2$ (1 mmol dm^{-3} in DMF), quantitatively formed in a mixture of $Pd(dba)_2 + 2PPh_3$, was characterized by UV spectroscopy with its absorption band at $\lambda_{max} = 396$ nm (Figure 1a). Addition of increasing amounts of PPh_3 resulted in a decay of the adsorption band of $Pd(dba)(PPh_3)_2$ due to the equilibrium with $Pd(0)(PPh_3)_3$ (eq 10) (Figure 1a).[2,5] The complex $Pd(dba)(TFP)_2$ (1 mmol dm^{-3} in DMF), quantitatively generated in mixtures of $Pd(dba)_2$ + 2TFP, was characterized by an adsorption band at ca. 390 nm, less well-defined than that of $Pd(dba)(PPh_3)_2$ (compare Figures 1a and b). Addition of increasing amounts of TFP resulted in a decay of the absorbance due to the equilibrium with $Pd(0)(TFP)_3$ (eq 8). It was qualitatively observed that for the same amount of added phosphine, the relative concentration of the complex $Pd(0)(dba)L_2$ was smaller when L = TFP. This suggests that $Pd(0)L_3$ is more stable vis à vis $Pd(0)(dba)L_2$ for TFP than for PPh_3. In other words, $K_0^{TFP} > K_0^{PPh_3}$. In DMF, the equilibrium constant $K_0^{PPh_3} = 0.16 \pm 0.02$ had been calculated from UV data.[5] Although the calculation was less precise for TFP, the value of the equilibrium constant K_0^{TFP} could be determined at $\lambda = 410$ nm, where C_0 is the initial concentration of $Pd(dba)_2$, n the number of equivalents of TFP relative to $Pd(dba)_2$, and $x = (D_0 - D_{eq})/(D_0 - D_\infty)$ (D_0 = initial absorbance of $Pd(0)(dba)(PPh_3)_2$, D_{eq} = absorbance at the equilibrium position, D_∞: absorbance when the equilibrium is totally shifted to its right-hand side). $K_0^{TFP} = 0.40 \pm 0.05$. Thus, the substitution of dba by the phosphine in $Pd(dba)L_2$ to form $SPdL_3$ is easier for L = TPF than for L = PPh_3. These results confirm what we have previously reported: dba is more easily substituted by the phosphine in $Pd(dba)L_2$ to form PdL_3 when the phosphine is more electron deficient.[5]

$$Pd(0)(dba)(PPh_3)_2 + PPh_3 \rightleftarrows SPd(0)(PPh_3)_3 + dba \qquad K_0^{PPh_3} \quad (10)$$

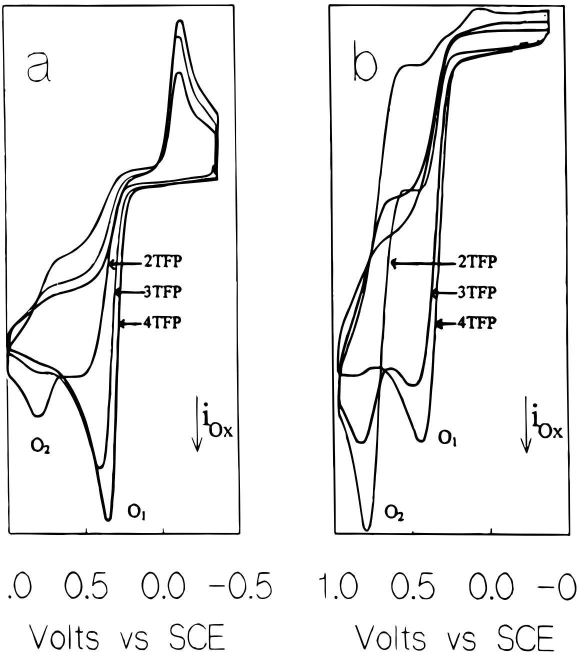


Figure 2. Cyclic voltammetry of a mixture of $Pd(dba)_2$ (2 mmol dm^{-3}) and n equiv of TFP (n = 2, 3, 4) at a stationary gold disk electrode (i.d. = 0.5 mm) with a scan rate of 0.2 V s^{-1} at 20 °C: (a) in DMF (containing n-Bu_4NBF_4, 0.3 mol dm^{-3}), (b) in THF (containing n-Bu_4NBF_4, 0.3 mol dm^{-3}).

$$Pd(0)(dba)(TFP)_2 + TFP \leftrightarrows SPd(0)(TFP)_3 + dba \qquad K_0^{TFP} \quad (8)$$

at equil:

$$[Pd(dba)(TFP)_2] = C_0(1 - x);\ [TFP] = C_0(n - 2 - x)$$

$$[SPd(0)(TFP)_3] = C_0x;\ [dba] = C_0(1 + x)$$

$$K_0^{TFP} = \frac{[SPd(0)(TFP)_3][dba]}{[Pd(dba)(TFP)_2][TFP]}$$

$$K_0^{TFP} = \frac{x(1 + x)}{(1 - x)(n - 2 - x)}$$

Identification of the Palladium(0) Complexes Formed in Situ in a Mixture of $Pd(dba)_2$ + nTFP ($n \geq 2$) in DMF and THF as Investigated by Cyclic Voltammetry. As already reported for mixtures of Pd-

Table 2. Oxidation Peak Potentials (E^p)^a of the Palladium(0) Complexes Generated in Situ in Mixtures of Pd(dba)$_2$ and nTFP (n > 2)

solvent	Pd(0)(TFP)$_3$ $E^p{}_{O_1}$ (V vs SCE)	Pd(0)(dba)(TFP)$_2$ $E^p{}_{O_2}$ (V vs SCE)
DMF	+0.34	+0.72
THF	+0.38	+0.77

^{a} Determined at 0.2 V s^{-1} at a stationary gold disk electrode (i.d. = 0.5 mm) in solvent containing n-Bu$_4$NBF$_4$ (0.3 mol dm^{-3}), 20 °C; [Pd(dba)$_2$] = 2 mmol dm^{-3}.

(dba)$_2$ + 2PPh$_3$,[2] cyclic voltammetry performed on a solution of Pd(dba)$_2$ (2 mmol dm^{-3}) and 2 equiv of TFP, in DMF or THF (containing n-Bu$_4$NBF$_4$, 0.3 mol dm^{-3}), exhibited two oxidation peaks O$_1$ and O$_2$ (Figure 2). Peak O$_2$ characterizes the complex Pd(dba)(TFP)$_2$, whereas the plateau-shaped one O$_1$ characterizes Pd(TFP)$_2$ involved in an equilibrium (CE mechanism[10]) with Pd(dba)(TFP)$_2$ as for PPh$_3$, eq 11.[2]

$$\underset{O_2}{\mathrm{Pd(0)(dba)(TFP)_2}} + S \rightleftarrows \underset{O_1}{S\mathrm{Pd(0)(TFP)_2}} + \mathrm{dba} \qquad K_1{}^{\mathrm{TFP}} \tag{11}$$

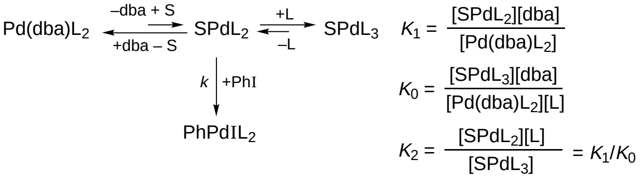
In the presence of more than 2 equiv of TFP per Pd(dba)$_2$, the magnitude of peak O$_1$ increased at the expense of that of O$_2$ (Figure 2), showing that the complex Pd(TFP)$_3$ was formed at the expense of Pd(dba)(TFP)$_2$ according to equilibrium 8. The two complexes

$$\underset{O_2}{\mathrm{Pd(0)(dba)(TFP)_2}} + \mathrm{TFP} \rightleftarrows \underset{O_1}{S\mathrm{Pd(0)(TFP)_3}} + \mathrm{dba} \qquad K_0{}^{\mathrm{TFP}} \tag{8}$$

SPd(0)(TFP)$_3$ and SPd(0)(TFP)$_2$ are oxidized at the same wave O$_1$ because they are involved in a fast equilibrium (eq 9) (CE mechanism[10]).[2,11] A comparison with PPh$_3$[2] evidences that palladium(0) complexes ligated by TFP are less easily oxidized than those ligated by PPh$_3$ (Table 2). This indicates that palladium(0) complexes are more electron rich when ligated by PPh$_3$. In other words, PPh$_3$ is more electron rich than TFP.[7b,9b,12,13]

A comparison with PPh$_3$ also shows that for the same ligand ratio, i.e., same value of n and for the same scan rate (0.2 V s^{-1}), the ratio i_{ox}(O$_1$)/i_{ox}(O$_2$) is always higher for TFP than for PPh$_3$. As soon as 4 equiv of TFP per Pd(dba)$_2$ was added, peak O$_1$ was detected alone, whereas for 4 equiv of PPh$_3$, both peaks O$_1$ and O$_2$ still coexisted (compare Figure 2 in this work with Figure 3 of ref 2). This suggests that $K_0{}^{\mathrm{TFP}} > K_0{}^{\mathrm{PPh_3}}$ and $K_1{}^{\mathrm{TFP}} > K_1{}^{\mathrm{PPh_3}}$.[14]

Scheme 2



Comparative Reactivity of the Palladium(0) Complexes Formed in Situ in Mixtures of Pd(dba)$_2$ + nTFP and Pd(dba)$_2$ + nPPh$_3$ (n ≥ 2). Kinetics of the Oxidative Addition with Phenyl Iodide. As already reported, the reactivity of palladium(0) complexes in oxidative additions is easily monitored by amperometry performed at a rotating disk electrode.[2,4,5] However, this method could not be used for the ligand TFP, due to a systematic pollution of the rotating disk electrode. Thus, the kinetics of the oxidative addition of the palladium(0) complexes generated in mixtures of Pd(dba)$_2$ + nTFP (n = 2, 4, and 10) with PhI was monitored by performing cyclic voltammetry at a steady electrode as a function of time (the electrode being polished just before each voltammogram was performed). The oxidative addition was investigated under stoichiometric conditions to achieve reasonable reaction times compatible with the duration between two voltammograms (ca. 1 min). The oxidation currents being proportional to the concentration of the palladium(0) complexes, the ratio i/i_0 = [Pd]/[Pd]$_0$ (i = oxidation peak current of O$_1$ at t, i_0 = initial oxidation peak current of O$_1$) was plotted as a function of time (Figure 3a) for different values of n and for both TFP and PPh$_3$ to allow comparison. The respective values of the half-reaction times $t_{1/2}$ are collected in Table 3.

As expected, the higher n, the slower the oxidative addition, for both ligands and both solvents (Figure 3a and Table 3). However, for identical values of n, one observes that in THF the oxidative addition is faster for PPh$_3$ when n = 2 or 4 whereas at higher n (n = 10) the reaction is faster for TPF. Therefore, depending on the ratio n = L/Pd, the order of reactivity can be reversed (Figure 3). In DMF, the oxidative addition is always faster for TFP than for PPh$_3$, whatever the value of n (n ≥ 2) (Table 3).

In the previous paper concerning PPh$_3$,[2] the mechanism of the oxidative addition was established and the reactive species in the oxidative addition identified as SPd(0)(PPh$_3$)$_2$ (Scheme 2).

When the concentration of Pd(dba)$_2$ and PhI are the same and when the ligands L and dba are in excess, the kinetic law is expressed as eq 12, where C_0 is the

$$1/x = k_{\mathrm{app}} C_0 t + 1 \tag{12}$$

initial concentration of palladium(0), $x = i/i_0$ = [Pd]/[Pd]$_0$, and k_{app} is the apparent rate constant of the overall reaction. Plotting the variation of 1/x as a function of time for 10 equiv of TFP per palladium and different concentrations of dba results in a series of straight lines that go through 1 (Figure 4a). This shows that the reaction order in PhI and Pd(0) is 1, and k_{app}

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[10] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 443.

[11] Amatore, C.; Jutand, A.; Medeiros, M. J.; Mottier, L. *J. Electroanal. Chem.* **1997**, *422*, 125.

[12] Although to our knowledge, the pK of the tri-2-furylphosphine is not reported, it is admitted that this ligand is less basic than PPh$_3$.[7b,9b]

[13] We noticed that in THF, the oxidation peak O′$_1$ assigned to the nonsolvated palladium(0) complex Pd(PPh$_3$)$_3$ in equilibrium with the solvated complex[2]

$$\underset{O'_1}{\mathrm{Pd(PPh_2)_3}} + \mathrm{TFP} \rightleftharpoons \underset{O_1}{\mathrm{(THF)Pd(0)(PPh_3)_3}} \qquad K_S{}^{\mathrm{PPH_3}}$$

was not detected for the palladium(0) complex ligated by TFP (compare Figure 2b here with Figure 3c in ref 2). This means that $K_S{}^{\mathrm{TFP}} \gg K_S{}^{\mathrm{PPh_3}}$ and also suggests that the palladium(0) complex ligated by TFP is less electron rich than that ligated by PPh$_3$.

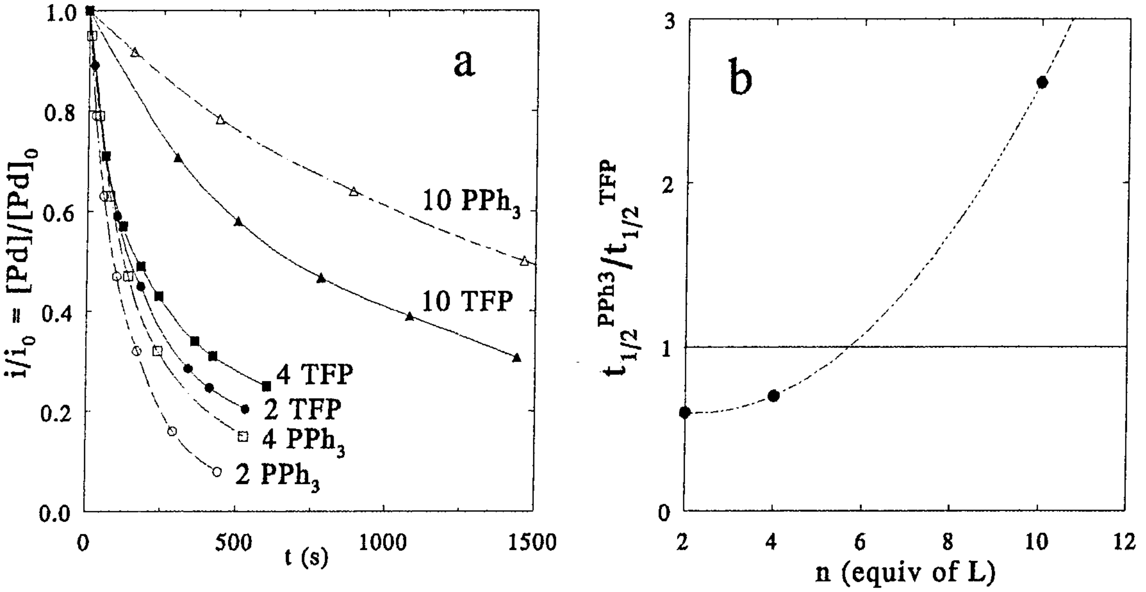

Figure 3. (a) Kinetics of the oxidative addition of PhI (2 mmol dm^{-3}) with the palladium(0) complexes generated in situ from mixtures of Pd(dba)$_2$ (2 mmol dm^{-3}) + n equiv of TFP (—) (n = 2, 4, 10) and from Pd(dba)$_2$ (2 mmol dm^{-3}) + n equiv of PPh$_3$ (- - -) (n = 2, 4, 10), monitored by cyclic voltammetry at a stationary gold disk electrode (i.d. = 0.5 mm) with a scan rate of 0.5 V s^{-1} in THF (containing n-Bu$_4$NBF$_4$, 0.3 mol dm^{-3}) at 20 °C. Plot of i/i_0 = [Pd]/[Pd]$_0$ (i = oxidation peak current of O$_1$ at t, i_0 = initial oxidation peak current) as a function of time. (b) Plot of the ratio $t_{1/2}{}^{\mathrm{PPh_3}}/t_{1/2}{}^{\mathrm{TFP}}$ as a function of n, in THF.

Table 3. Determination of the Half-Reaction Time $t_{1/2}$ of the Oxidative Addition of PhI with the Palladium(0) Complexes Generated in Situ in Mixtures of Pd(dba)$_2$ and nL ($n \geq 2$) at 20 °C[a]

	$t_{1/2}$ (s)					
	2L		4L		10L	
solvent	PPh$_3$	TFP	PPh$_3$	TFP	PPh$_3$	TFP
DMF	195	110	280	190	1650	640
THF	86	143	120	170	1800	690

[a] [PhI] = [Pd(dba)$_2$] = 2 mmol dm^{-3}.

was calculated from the slopes of the regression lines. The reaction went slower and slower when the concentration of dba was increased. This demonstrates that the reactive species in the oxidative addition is involved in an equilibrium with dba, as postulated in Scheme 2.

The apparent rate constant k_{app} is expressed as eq 13[2]

$$k_{\mathrm{app}} = \frac{k}{1 + [\mathrm{dba}]/K_1 + [\mathrm{TFP}]/K_2} \qquad (13)$$

or

$$\frac{1}{k_{\mathrm{app}}[\mathrm{TFP}]} = \left\{\frac{1}{k[\mathrm{TFP}]} + \frac{1}{kK_2}\right\} + \frac{[\mathrm{dba}]}{kK_1[\mathrm{TFP}]} \qquad (14)$$

When 1/k_{app}[TFP] was plotted as a function of [dba]/[TFP] (eq 14), a straight line was obtained (Figure 4b) whatever the TFP concentration, showing that 1/k[TFP] is always very small compared to 1/kK_2 and to experimental uncertainty, i.e., $k > 50$ M^{-1} s^{-1}. In THF, kK_2 = (4.2 ± 0.1) × 10^{-2} s^{-1} was calculated from the intercept whereas kK_1 = (1.07 ± 0.01) × 10^{-2} s^{-1} was calculated from the slope. Then, $K_0 = K_1/K_2 = 0.26 \pm 0.01$. The same calculation was made in DMF (Table 4) and the results compared to those already reported for PPh$_3$[2] (Table 4). In both solvents, $K_0{}^{\mathrm{TFP}} > K_0{}^{\mathrm{PPh_3}}$ but the effect is more important in DMF.

In the absence of any added dba, the oxidative addition, when performed under stoichiometric conditions, follows the kinetic laws, eqs 15 and 16. In THF,

$$\text{For } n = 2\text{:}\quad 1/x + {}^1\!/_2 \ln x = {}^1\!/_2 k^{\mathrm{L}} K_1{}^{\mathrm{L}} t + 1 \qquad (15)$$

$$\text{For } n = 4\text{:}\quad 1/x + ({}^1\!/_2 \ln x)/(1 + K_0{}^{\mathrm{L}}) = (k^{\mathrm{L}} K_1{}^{\mathrm{L}} t)/(2(K_0{}^{\mathrm{L}} + 1)) + 1 \qquad (16)$$

when n = 2, a plot of $1/x + {}^1\!/_2 \ln x$ as a function of time gave a straight line (Figure 5) which goes through 1 (eq 15). The value of $k^{\mathrm{L}}K_1{}^{\mathrm{L}}$ has been calculated from the slope ($k^{\mathrm{TFP}}K_1{}^{\mathrm{TFP}}$ = 1.08 × 10^{-2} s^{-1} in THF) and agrees perfectly with the value calculated above.

When n = 4, the kinetic law depends on $K_0{}^{\mathrm{L}}$ (eq 16), which has already been determined as reported above (Table 4). Using this value, one plots the variation of $1/x + ({}^1\!/_2 \ln x)/(1 + K_0{}^{\mathrm{L}})$ as a function of time (eq 16). The value of $k^{\mathrm{L}}K_1{}^{\mathrm{L}}$ is calculated from the slope of the straight line (Figure 5). $k^{\mathrm{TFP}}K_1{}^{\mathrm{TFP}}$ = 1.06 × 10^{-2} s^{-1} in THF, which again compares excellently with the above determination. In THF, the values of $k^{\mathrm{TFP}}K_1{}^{\mathrm{TFP}}$ calculated by three different kinetic laws are very similar and, thus, confirm the mechanism proposed in Scheme 2. Similar analysis of the kinetics of the oxidative addition performed in DMF allows the determination of $k^{\mathrm{TFP}}K_1{}^{\mathrm{TFP}}$ and comparison with $k^{\mathrm{PPh_3}}K_1{}^{\mathrm{PPh_3}}$ (Table 4).

Final Discussion and Conclusion

As recalled in the Introduction, the overall reactivity of {Pd(dba)$_2$ + nL} in the oxidative addition is determined by the intrinsic reactivity of the reactive species Pd(0)L$_2$ in the elementary step of the oxidative addition (i.e., k in eq 5) and also by its concentration which is controlled by K_1 and K_0. K_0 (eq 3) plays a special role

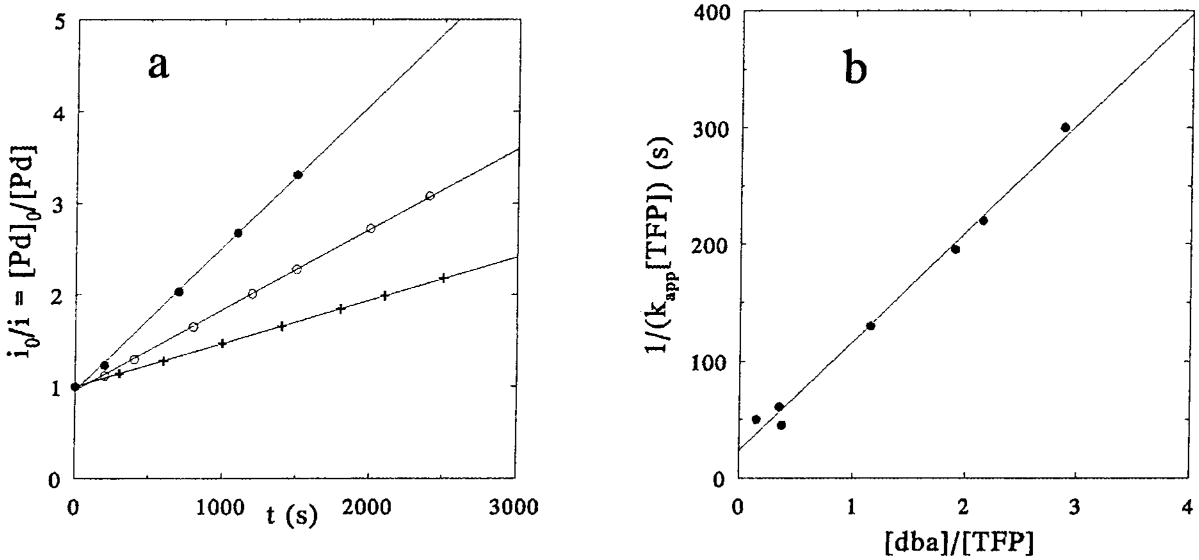

Figure 4. Kinetics of the oxidative addition of PhI (2 mmol dm^{-3}) with the palladium(0) complex generated in situ from a mixture of $Pd(dba)_2$ (2 mmol dm^{-3}) + 10 equiv of TFP in THF (containing n-Bu_4NBF_4, 0.3 mol dm^{-3}) as a function of the dba concentration. (a) Plot of $i_0/i = [Pd]_0/[Pd]$ as a function of time and the amount of added dba: (●) 0, (○) 10, (+) 20 equiv of dba, 20 °C. (b) Plot of $1/k_{app}[TFP]$ as a function of [dba][TFP], $\rho = 0.996$ (see eq 14).

Table 4. Determination of the Equilibrium Constants and Kinetic Parameters for Palladium(0) Complexes Generated in Situ in Mixtures of $Pd(dba)_2$[a] and nL ($n \geq 2$) and Involved in the Oxidative Addition with PhI, According to Scheme 2

	$10^2 \times k^L K_1^L$ (s^{-1})		$10^2 \times k^L K_2^L$ (s^{-1})		K_0^L	
solvent	PPh_3[b]	TFP	PPh_3[b]	TFP	PPh_3[b]	TFP
DMF	0.63 ± 0.01	1.13 ± 0.01	4.6 ± 0.4	1.74 ± 0.1	0.14 ± 0.03 0.16 ± 0.02[c,d]	0.32 ± 0.03 0.40 ± 0.05[d]
THF	1.10 ± 0.01	1.07 ± 0.01	4.75 ± 0.1	4.2 ± 0.1	0.23 ± 0.03	0.26 ± 0.01

[a] $[Pd(dba)_2] = 2$ mmol dm^{-3}, 20 °C. [b] Reference 2. [c] Reference 5. [d] Calculated from UV data (see text).

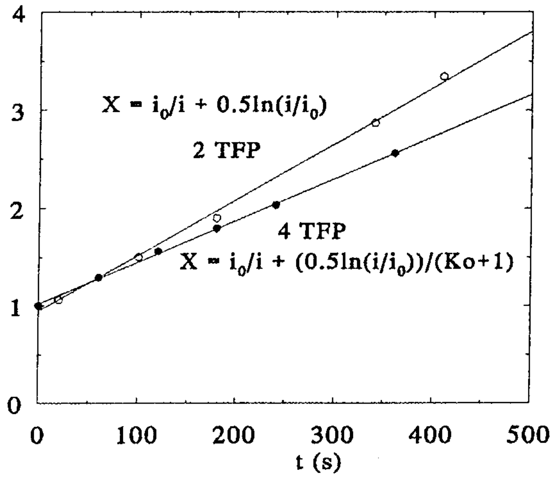

Figure 5. Kinetics of the oxidative addition of PhI (2 mmol dm^{-3}) with the palladium(0) complex generated in situ from mixtures of $Pd(dba)_2$ (2 mmol dm^{-3}) + n equiv of TFP in THF (containing n-Bu_4NBF_4, 0.3 mol dm^{-3}). $i_0/i = [Pd]_0/[Pd]$; n = (○) 2 (see eq 15), (●) 4 (see eq 16), 20 °C.

since it reflects the ratio of the only species $SPd(0)L_3$ and $Pd(0)(dba)L_2$ present at macroscopic concentration. Either K_1 (eq 2) or K_2 (eq 4) can be used to describe the relative concentration of $SPd(0)L_2$, the true reactive species present at trace amounts. Ideally, K_1 (i.e., $SPd(0)L_2$ vs $Pd(0)(dba)L_2$) should be used when $K_0[L]/[dba] \ll 1$ (i.e., when $Pd(dba)L_2$ is the major species), and K_2 (i.e., $SPd(0)L_2$ vs $SPd(0)L_3$) should be used when $K_0[L]/[dba] \gg 1$ (i.e., when $SPdL_3$ is the major species). Under the usual catalytic conditions where L is not in great excess, $Pd(0)(dba)L_2$ dominates over $SPd(0)L_3$ so that it is reasonable to use the pair K_1, K_0 to describe the system while keeping in mind that $K_2 = K_1/K_0$.

When compared to PPh_3, TFP is less electron rich, and consequently, the intrinsic reactivity (viz. the rate constant) of $SPd(TFP)_2$ in the oxidative addition (eq 5) should be less than that of $SPd(PPh_3)_2$ with $k^{TFP} < k^{PPh_3}$. But from the data collected in Table 4, one observes that in DMF and THF, $K_0^{TFP} > K_0^{PPh_3}$. Thus, two antagonist effects might be involved.

In THF, at low n ($n = 2$), the overall reactivity of $\{Pd(dba)_2 + nL\}$ (viz. the rate constant times the concentration) is controlled by $k^L K_1^L$ (eq 15) and the complex ligated by PPh_3 is more reactive than that ligated by TFP (Figure 3a, Table 3). K_1^L cannot be calculated. However, from the cyclic voltammetry,[14] we are inclined to conclude that $K_1^{PPh_3} < K_1^{TFP}$, i.e., the concentration of $Pd(0)(PPh_3)_2$ is less than that of $Pd(0)(TFP)_2$ but $Pd(0)(PPh_3)_2$ is more reactive than $Pd(0)(TFP)_2$. As a result of these two antagonist effects, $k^{PPh_3}K_1^{PPh_3}$ is found to be slightly superior to $k^{TFP}K_1^{TFP}$, which means that k^{PPh_3} is considerably much higher than k^{TFP} and thus k is more determinant than K_1. In other words,

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[14] Although the magnitude of the peak current does not represent the true concentration of the species but a dynamic concentration,[2,10] due to equilibrium 8, one concludes that either $K_0^{TFP} > K_0^{PPh_3}$ (which was established from UV spectroscopy) or that equilibrium 8 is more easily shifted to $Pd(0)(TFP)_3$ than it is to $Pd(0)(PPh_3)_3$ when the species is continuously oxidized in the diffusion layer or both. The same conclusions are drawn for equilibrium 11 and K_1.

the relative rate of the intrinsic oxidative addition (k) is more important than is the ability of the solvent to displace dba from Pd(dba)L_2 to form SPdL_2.

At higher values of n ($n > 2$), equilibrium 3 (K_2) has to be considered and consequently K_0 with on the one hand $K_0^{\mathrm{PPh_3}} < K_0^{\mathrm{TFP}}$ and on the other hand $k^{\mathrm{PPh_3}} > k^{\mathrm{TFP}}$, i.e., still two antagonist effects. The concentration of the reactive species Pd(0)L_2 is modulated by the values of n and K_0. Even if Pd(0)(TFP)$_2$ is less reactive than Pd(0)(PPh$_3$)$_2$, its concentration is considerably higher than that of Pd(0)(PPh$_3$)$_2$ when n is large, resulting in a higher overall reactivity. Due to these two antagonist effects, an inversion of the reactivity order occurs when n increases. This was observed when switching from $n = 4$ to $n = 10$ (Table 3, Figure 3a). The ratio $t_{1/2}^{\mathrm{PPh_3}}/t_{1/2}^{\mathrm{TFP}}$ was plotted versus n (Figure 3b). Its value is 1 (same overall reactivity for both ligands) when $n \approx 6$. Thus, when $n > 6$, the catalytic system with TPF is more reactive than that with PPh$_3$, whereas the reverse is observed for $n < 6$.

In DMF, the system {Pd(dba)$_2$ + nTFP} is found to be more reactive than {Pd(dba)$_2$ + nPPh$_3$}, whatever n ($n \geq 2$). In this solvent when $n = 2$, $k^{\mathrm{TFP}}K_1^{\mathrm{TFP}} > k^{\mathrm{PPh_3}}K_1^{\mathrm{PPh_3}}$ (Table 4). Since $k^{\mathrm{TFP}} < k^{\mathrm{PPh_3}}$, this means that the contribution of K_1^{TFP} which controls the concentration of Pd(0)(TFP)$_2$ is more important than that of k^{TFP} (the reverse effect was observed in THF, see above). For $n > 2$, K_0 is involved with $K_0^{\mathrm{TFP}} > K_0^{\mathrm{PPh_3}}$. Thus, as for K_1^{TFP}, the contribution of K_0^{TFP} is more important than that of k^{TFP}. Despite the fact that TFP is less basic than PPh$_3$, the overall oxidative addition is faster with TFP because the concentration of SPd(TFP)$_2$ is always higher than that of SPd(PPh$_3$)$_2$, whatever n ($n \geq 2$).

In practice, in THF, one generally uses a mixture of Pd(dba)$_2$ + nL with $n = 2$ or 4.[6a,b,d,e,g,h] From the results reported above, the mixtures {Pd(dba)$_2$ + nTFP} ($n = 2$ or 4) are slightly less reactive than {Pd(dba)$_2$ + nPPh$_3$} ($n = 2$ or 4) in oxidative additions. Thus, the fact that the rate of a palladium-catalyzed reaction involving an oxidative addition with ArX is considerably enhanced when switching from PPh$_3$ to TFP[6a,b,e,g] does not originate from the oxidative addition. As a consequence, in this case, this step cannot be the rate-determining step of the catalytic cycle.[7b] The higher rate probably originates from a further step, for example, the nucleophilic attack (transmetalation) on arylpalladium(II) complexes which are more electron deficient when ligated by TFP than by PPh$_3$.

In DMF,[6c,i] the results differ since the oxidative addition is always faster with TFP than with PPh$_3$. Thus, in this solvent, both the oxidative addition and the nucleophilic attack should be enhanced when using TFP instead of PPh$_3$.

Experimental Section

^{31}P NMR spectra were recorded in DMF on a Bruker spectrometer (101 MHz) using 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 oscilloscope.

Reagents. All experiments were performed under argon. DMF (Acros) was distilled over calcium hydride under vacuum and stored under an argon atmosphere. THF (Acros) was distilled from sodium benzophenone. The solvent was transferred to the cells according to standard Schlenk procedures. The tri-2-furylphosphine was commercial grade (Strem Chemical) and used without further purification. Phenyl iodide (Acros) was filtered on neutral alumina and stored under argon. The bis(dibenzylidenacetone)palladium(0) was synthesized according to published procedures.[15]

^{31}P NMR Experiments. A 3.7 mg (0.0064 mmol) amount of Pd(dba)$_2$ was introduced into an NMR tube containing 0.5 mL of DMF or THF and 0.05 mL of acetone-d_6, followed by the suitable amount of TFP (2 or 4 equiv relative to Pd(dba)$_2$). In another experiment, phenyl iodide (10 equiv) was added to the mixture of Pd(dba)$_2$ and nTFP ($n = 2$ or 4).

UV Experiments. The UV spectroscopy was performed in DMF or THF in a thermostated 1 mm path length cell on mixtures of Pd(dba)$_2$ (2 mmol dm^{-3}) and the suitable amount of TFP (4−100 mmol dm^{-3}).

Electrochemical Experiments. These studies were carried out in a three-electrode cell connected to a Schlenk line. The cell was equipped with a double envelope to have a constant temperature of 20 °C (Lauda RC20 thermostat). The working electrode consisted of a gold disk of 0.5 mm diameter. 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 a solution of n-Bu$_4$NBF$_4$ (0.3 mol dm^{-3}) in 3 mL of DMF or THF. A 12 mL amount of DMF or THF containing the same concentration of supporting electrolyte was poured into the cell. A 13.6 mg amount of Pd(dba)$_2$ (0.024 mmol) was then added, followed by the suitable amount of TFP. Cyclic voltammetry was performed at a scan rate of 0.2 V s^{-1}. The kinetic measurements were performed by cyclic voltammetry at a scan rate of 0.5 V s^{-1} in the presence of 2.7 μL (0.024 mmol) of phenyl iodide.

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