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Role of dba in the reactivity of palladium(0) complexes generated in situ from mixtures of $Pd(dba)_2$ and phosphines

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Contents

Abstract

The ligand dba plays a crucial role both on the structure and on the reactivity of palladium(0) complexes generated in situ in mixtures of $Pd(dba)_2$ and phosphine ligands. Whatever the ligand, the major complex is always $Pd(dba)L_2$ where L is a monodentate phosphine ligand or Pd(dba)(L–L) where L–L is a bidentate phosphine ligand. In all cases, the most reactive species in the oxidative addition with phenyl iodide is the lowest ligated complex PdL_2 or Pd(L–L) in equilibrium with the major complex and dba. However, Pd(dba)(L–L) also reacts with phenyl iodide. The presence of the major complexes ligated by dba diminishes the concentration of the more reactive species PdL_2 or Pd(L–L) and consequently controls

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the rate of the overall reaction. The overall reactivity is governed both by the intrinsic reactivity of the reactive species and its concentration, two factors which can be antagonistic and a non-linear Hammett correlation of the oxidative addition with the basicity of the phosphine is observed for monodentate ligands.

Keywords: Palladium(0); *trans,trans*-dibenzylideneacetone; Oxidative addition

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1. Introduction

Palladium is the most efficient catalyst in reactions involving aryl halides [1–7] and triflates [1–8], vinyl halides [1–7] and triflates [8], acyl halides [1–7], allylic acetates [4,9,10] and carbonates [4,11]. All these reagents can be catalytically activated by palladium(0) complexes *via* an oxidative addition, which consists in the first step of the pertinent catalytic cycle. Considering the stable complex $Pd(0)(PPh_3)_4$, it has been established in 1980, that the real complex active in the oxidative addition is the 14 electron low ligated complex $Pd(0)(PPh_3)_2$ resulting from two successive deligations of PPh_3 from the saturated 18 electron complex [12]. Among all the palladium(0) sources, susceptible to afford active 14 electron complexes, $Pd(0)L_2$ (L = monodentate phosphine ligand) or Pd(0)(L–L) (L–L = bidentate phosphine ligand), mixtures of $Pd(0)(dba)_2$ (dba = *trans,trans*-dibenzylideneacetone) associated to monodentate [13–54] or bidentate [49–87] phosphine ligands are commonly used. The first catalytic system, $Pd(0)(dba)_2 + 2DIOP$, was tested in 1978, in catalytic nucleophilic substitutions on allylic acetates [69]. The twin objective was: (i) to have a convenient method for the generation in situ of the palladium(0) complex $Pd(DIOP)_2$ since dba was supposed to be a very labile ligand and (ii) to generate a chiral center prone to induce enantioselective reactions. Since then, this method has proved to be very efficient in synthesis [13–87]. Indeed, the complex $Pd(dba)_2$ is very air stable, considerably more stable than other palladium(0) complexes such as $Pd(PPh_3)_4$. Under such conditions, one by-passes the synthesis of phosphine ligated palladium(0) complexes which are air sensitive. Moreover, in such catalytic systems, one can easily vary at will the phosphine ligand and examine the influence of the ligand on the catalytic reactions, in terms of reactivity and/or enantioselectivity. As a consequence, albeit chiral aspects are lost, catalytic systems involving mixtures of $Pd(dba)_2 + 4PPh_3$ have been tested in catalytic reactions. Indeed they were expected to afford in situ $Pd(PPh_3)_4$. However, when looking carefully at the literature, one observes that the reactivity of $Pd(PPh_3)_4$ in catalytic reactions differs from that of $Pd(dba)_2 + 4PPh_3$. $Pd(PPh_3)_4$ is sometimes the most efficient catalyst and is even more reactive than mixtures of $Pd(dba)_2 + 2PPh_3$ [20,22,23,27,31]. This suggests that $Pd(dba)_2 + 4PPh_3$ is not equivalent to $Pd(PPh_3)_4$ and that dba, expected to be a very labile ligand, could play a role as ligand in catalytic reactions. In order to clarify the role of the ligand dba, mixtures of $Pd(dba)_2 + n$L or n'L–L, were investigated from a kinetic point of view, to characterize the different palladium(0) complexes present in solution and to determine the reactive species in oxidative addition [88–91]. Phenyl iodide was chosen as a common model compound for the oxidative addition.

Electrochemical techniques such as cyclic voltammetry, chronoamperometry and steady state amperometry were used to determine the number of palladium(0) complexes present in solution (by detection of their oxidation peaks) and their concentration (the oxidation current of a species is proportional to its concentration). The release in solution of the dba ligand(s) when phosphine ligands were added to $Pd(dba)_2$ could also be simultaneously monitored by observation of the reduction peaks of dba. These electrochemical techniques were crucial to characterize the thermodynamics of the possible equilibrium between the different palladium(0) complexes and to monitor their individual reactivity in oxidative additions, allowing the identification of the most reactive species. Although these electrochemical techniques allow detailed investigations of mechanistic features, they cannot provide any structural information on the structure of the different complexes (unless by comparison to authentic samples) and complementary spectroscopic methods are needed such as ^{31}P NMR and UV spectroscopy.

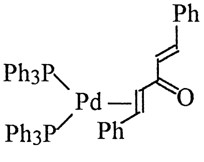
We review hereafter our results concerning the characterization, in terms of structure and reactivity, of mixtures of $Pd(dba)_2$ with monodentate or bidentate phosphine ligands. The principles and *modus operandi* of our mechanistic approach will be developed in detail for $L = PPh_3$, as an example.

2. Mixtures of $Pd(dba)_2$ and monodentate phosphines, L

2.1. Mixtures of $Pd(dba)_2 + nPPh_3$ ($n \geq 2$)

2.1.1. Mixtures of $Pd(dba)_2 + 2PPh_3$

^1H NMR spectra of $Pd(dba)_2$ in chloroform-d_1, showed one free and one ligated dba. A ^{31}P NMR spectrum performed on a solution of $Pd(dba)_2$ and $2PPh_3$ in THF or DMF exhibited two signals of equal amplitude characteristic of two different phosphorous atoms (Fig. 1(a)). These signals are assigned to the complex $Pd(dba)(PPh_3)_2$ in which a monoligation of the dba ligand on the palladium induces the presence of two non-equivalent phosphorous atoms [88,92].



$$Pd(0)(dba)_2 \rightarrow Pd(0)(dba) + dba \qquad (1)$$

$$Pd(0)(dba) + 2PPh_3 \rightarrow Pd(0)(dba)(PPh_3)_2 \qquad (2)$$

Cyclic voltammograms of $Pd(dba)_2$ ($2\ mmol\ dm^{-3}$) in the presence of 2 equiv. of PPh_3, in DMF or THF (containing n-Bu_4NBF_4, $0.3\ mol\ dm^{-3}$) exhibited two oxidation waves O_1 and O_2 (Fig. 2(a)). The major oxidation peak O_2 characterizes

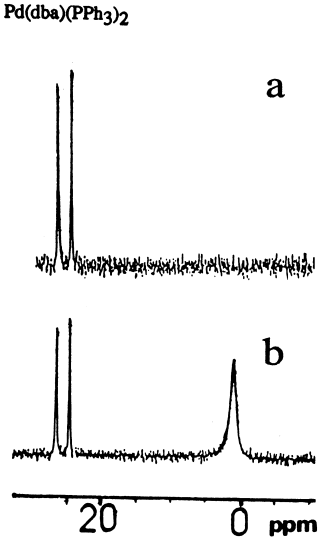


Fig. 1. ^{31}P NMR spectrum (162 MHz) performed in 3 mL of THF and 0.2 mL of acetone-d_6 with H_3PO_4 as an external reference. (a) $Pd(dba)_2$ (14 mmol dm^{-3})+2 equiv. of PPh_3. (b) $Pd(dba)_2$ (14 mmol dm^{-3})+4 equiv. of PPh_3.

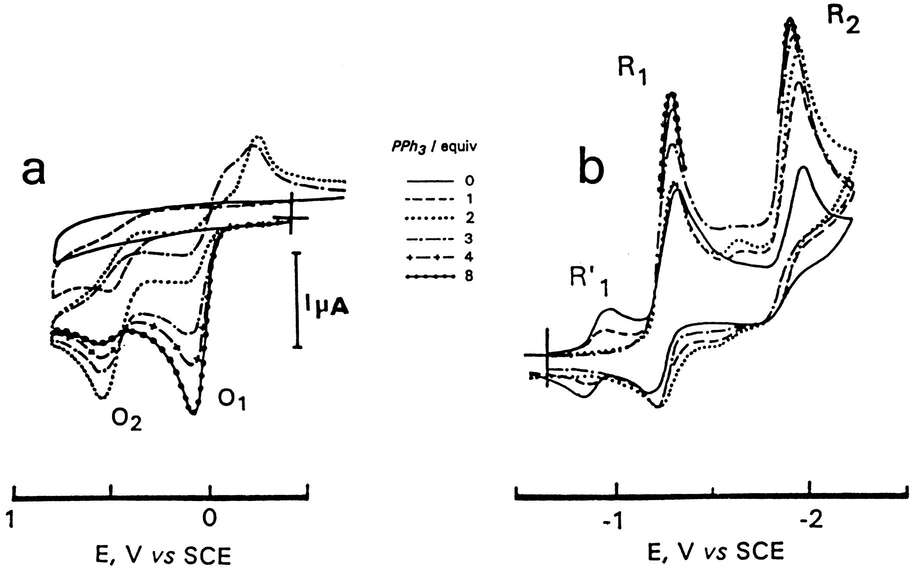


Fig. 2. Cyclic voltammetry performed in DMF (containing n-Bu_4NBF_4, 0.3 mmol dm^{-3}) at a stationary gold disk electrode (0.5 mm diameter) with a scan rate of 0.2 V s^{-1}. (a) Oxidation of $Pd(dba)_2$ (2 mmol dm^{-3}) in the presence of various equivalents n of added PPh_3 as shown in the insert. (b) Reduction of $Pd(dba)_2$ (2 mmol dm^{-3}) in the presence of various equivalents n of added PPh_3 as shown in the insert.

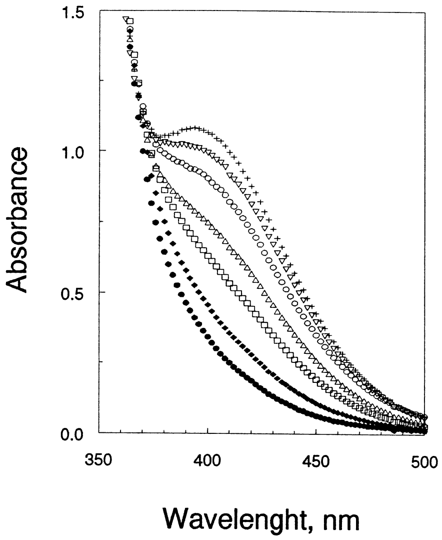


Fig. 3. UV spectroscopy performed in DMF in a 1 mm path cell at 20 °C. $Pd(dba)_2$ (0.1 mmol dm^{-3})+$n$$PPh_3$; $n=2$ (+), 4 (▽), 6 (○), 10 (△), 20 (□), 50 (◆), 100 (●) equivalents.

the complex $Pd(dba)(PPh_3)_2$ whereas the plateau-shaped oxidation wave O_1 characterizes $Pd(PPh_3)_2$ involved in an equilibrium (CE mechanism [93]) with $Pd(dba)(PPh_3)_2$ (S=solvent) [88]:

$$\underset{O_2}{Pd(0)(dba)(PPh_3)_2} + S \rightleftarrows \underset{O_1}{SPd(0)(PPh_3)_2} + dba \quad K_1 \tag{3}$$

The complex $Pd(0)(dba)(PPh_3)_2$ could also be characterized by UV spectroscopy through observation of its absorption band at $\lambda_{max}=396$ nm, in DMF (Fig. 3) [90].

From these results, one may already conclude that the catalytic system $Pd(dba)_2+2PPh_3$ is not equivalent to $Pd(0)(PPh_3)_2$, since the major complex in solution is $Pd(dba)(PPh_3)_2$.

2.1.2. Mixtures of $Pd(dba)_2+nPPh_3$ ($n>2$)

When increasing amounts of PPh_3 were added to $Pd(dba)_2$, the two ^{31}P NMR signals characteristic of $Pd(0)(dba)(PPh_3)_2$ progressively disappeared and a broad signal appeared upperfield (Fig. 1(b)). In no case could the free ligand PPh_3 signal be observed. The broad upperfield signal characterizes palladium(0) complexes in equilibrium with the ligand PPh_3 (Eq. (4)) (the same behavior was observed upon progressive addition of PPh_3 to a solution of $Pd(PPh_3)_4$).

$$SPd(0)(PPh_3)_3 \rightleftarrows SPd(0)(PPh_3)_2 + PPh_3 \quad K_2 \tag{4}$$

When the cyclic voltammetry was performed in oxidation, the oxidation wave O_2 progressively disappeared upon increasing PPh_3 concentration, while the oxidation wave O_1 increased at its expense and became progressively peak-shaped (Fig. 2(a)).

Simultaneously, dba was released in solution as attested by the increase of its reduction peak currents at R_1 and R_2 (Fig. 2(b)). This demonstrates that complexes $Pd(0)(dba)(PPh_3)_2$ and $SPd(0)(PPh_3)_3$ are involved in an equilibrium with the phosphine and the dba ligands (Eq. (5)) [88]. The two complexes $SPd(0)(PPh_3)_3$ and $SPd(0)(PPh_3)_2$ are oxidized at the same potential O_1 because they are involved in a fast equilibrium (Eq. (4)).

$$\underset{O_2}{Pd(0)(dba)(PPh_3)_2} + PPh_3 \rightleftarrows \underset{O_1}{SPd(0)(PPh_3)_3} + dba \quad K_0 = K_1/K_2 \tag{5}$$

These results were also confirmed by UV spectroscopy since the absorption band characteristic of $Pd(0)(dba)(PPh_3)_2$ progressively disappeared when PPh_3 was gradually added to the solution (Fig. 3). The absorption band of $Pd(dba)(PPh_3)_2$ completely disappeared when at least 50 equivalents of PPh_3 were added to $Pd(dba)(PPh_3)_2$ (Fig. 3). This means that at least 50 equivalents of PPh_3 are necessary to completely displace dba from $Pd(dba)(PPh_3)_2$ [90]. Thus, the affinity of dba for $Pd(PPh_3)_2$ is considerably higher than that of PPh_3 and dba in $Pd(dba)(PPh_3)_2$ is not as labile as usually postulated. In other words, the first dba ligand is easily exchanged by two phosphine ligands, while the second one is hard to remove [94].

When the monodentate phosphine possesses a high cone angle, mixtures of $Pd(dba)_2 + nL$ ($n > 2$) results in the formation of $Pd(dba)L_2$. Due to the bulkiness of the ligand, more ligated complexes such as PdL_3 are not formed. The stable complex $Pd(dba)(PCy_3)_2$ has been isolated and characterized [92,95]. Similar behavior has also been observed with functional ligands such as $PPh_2CH_2C(O)Ph$ and the bis-ligated complex $Pd(dba)(PPh_2CH_2C(O)Ph)_2$ is only formed, even in the presence of excess ligand [96].

2.1.3. *Determination of K_0 and characterization of the reactive species in the oxidative addition*

The value of the equilibrium constant K_0 between $Pd(dba)(PPh_3)_2$ and $Pd(PPh_3)_3$ (Eq. (5)) has been determined by three independent techniques. The first one is chronoamperometry [88]. In cyclic voltammetry, we observed that the ratio of the oxidation currents of O_2 and O_1 varied with the concentration of PPh_3 but also with the scan rate. For a given concentration of PPh_3, i_{O1}/i_{O2} decreased when the scan rate increased, i.e. when the time scale decreased. This behavior is characteristic of two species in equilibrium, as in Eq. (5). The oxidation peak currents (usually proportional to the concentrations) are in fact not representative of the concentrations of the two complexes $Pd(dba)(PPh_3)_2$ and $Pd(PPh_3)_3$ in the bulk solution but of the dynamic concentrations resulting from the shifting of the equilibrium (Eq. (5)) to the right, by the continuous oxidation of $Pd(PPh_3)_3$ in the diffusion layer (CE mechanism [93]). For shorter and shorter times, the equilibrium is less and less shifted to the right by the oxidation of $Pd(PPh_3)_3$ until it is frozen. The same behavior occurs in chronoamperometry, therefore the oxidation currents were determined by chronoamperometry which allows, in this case, more precise measurements than cyclic voltammetry. The oxidation currents i_{O1} and $i_{O1} + i_{O2}$ were mea-

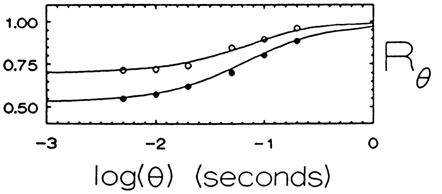


Fig. 4. Chronoamperometric oxidation of $Pd(dba)_2$ (2 mmol dm^{-3}) in DMF (containing n-Bu_4NBF_4, 0.3 mol dm^{-3}) in the presence of various amounts of added PPh_3, performed at gold disk electrodes (0.5 mm or 25 μm diameter) at 20 °C. Variations of $R_\theta = i_{O1}/(i_{O1}+i_{O2})$ as a function of the pulse duration θ and the phosphine concentration: $[PPh_3]_0 = 20$ (●), 40 (○) mmol dm^{-3}. The solid curves are the predicted variations simulated on the basis of the pertinent rate laws and rate constants [88].

sured by performing two series of potential steps of same duration θ, one on O_1 and the other on O_2. The ratio $R_\theta = i_{O1}/(i_{O1}+i_{O2})$ could thus be determined as a function of the duration θ of the potential steps and exhibited a plateau at short times (Fig. 4) while it tended towards unity at large θ values.

The limit unity corresponds to a complete lability of Eq. (5) in this time range, so that all palladium(0) centers are oxidized at O_1. Conversely, at short times, the equilibrium (Eq. (5)) is frozen so that the equilibrium constant K_0 is readily calculated from the value of the plateau (Table 1).

K_0 has also been determined by UV spectroscopy [90]. The absorbance D of $Pd(0)(dba)(PPh_3)_2$ involved in the equilibrium (Eq. (5)) was determined at $\lambda =$ 450 nm, from mixtures of $Pd(dba)_2 + nPPh_3$ ($n > 2$). The equilibrium constant was then calculated from the ratio $x = (D_0 - D)/(D_0 - D_\infty)$ (D = absorbance of $Pd(dba)(PPh_3)_2$ for a given value of n, D_0 = intrinsic absorbance of $Pd(dba)(PPh_3)_2$ determined for $n = 2$) for different values of n: $K_0 = x(1+x)/(1-x)(n-2-x)$ (Table 1).

The third route for the determination of K_0 was afforded by kinetic investigation of the reactivity of mixtures of $Pd(dba)_2 + nPPh_3$ ($n \geq 2$) in oxidative addition with phenyl iodide [88]. Steady state amperometry is the best technique to monitor the kinetics of the oxidative addition. A rotating disk electrode is polarized on the plateau of waves O_1 or O_2, i.e. on the oxidation waves of $SPd(PPh_3)_3$ or $Pd(dba)(PPh_3)_2$, and the decay of the oxidation current, featuring all palladium(0) complexes, is recorded as a function of time, after addition of PhI. The overall rate of the oxidative addition follows a kinetic law first order in PhI and first order in

Table 1
Determination of the equilibrium constant K_0 (Eq. (5)) at 20 °C by different techniques

Technique	K_0 DMF	THF
Chronoamperometry	0.16 ± 0.02	0.23 ± 0.03
UV spectroscopy	0.16 ± 0.02	n.d.
Steady state amperometry	0.140 ± 0.015	0.232 ± 0.007

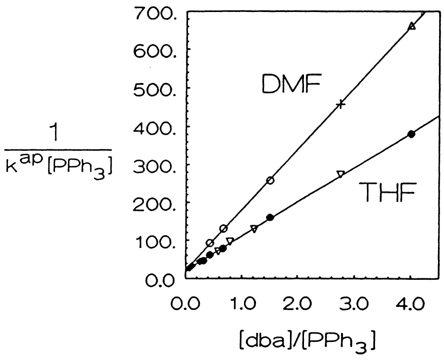
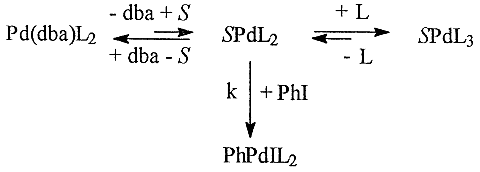


Fig. 5. Variations of the apparent rate constant, k_{app}, in ($M^{-1} s^{-1}$) of the oxidative addition of PhI (5 to 20 equiv.) with the palladium(0) generated from mixtures of $Pd(dba)_2$ (2 mmol dm^{-3}), dba and PPh_3, as a function of dba and PPh_3 concentrations, in DMF and THF (containing n-Bu_4NBF_4, 0.3 mol dm^{-3}). Initial concentration of $Pd(dba)_2$: 2 mmol dm^{-3}; concentration of added PPh_3: 10 to 80 mmol dm^{-3}; concentration in added dba: 0 (●), 20 (▽), 40 (◆) mmol dm^{-3} in THF and 20 (○), 40 (+), 60 (△) mmol dm^{-3} in DMF, at 20 °C.



Scheme 1. Mechanism of the oxidative addition

palladium(0) and the apparent rate constant of the oxidative addition varies with the concentration of dba and PPh_3, as in Fig. 5. The overall reaction is slower when the concentration of the phosphine and/or the concentration of dba increase. The kinetic curves and rate constants were identical whatever the polarization potential (e.g. on O_1 or on O_2) which means that all the equilibria involving palladium (0) complexes are totally labile during the time scale of the oxidative addition and could not be kinetically discriminated. The reactive species is the lowest ligated complex $\mathcal{S}Pd(PPh_3)_2$ involved in an equilibrium with the main species $\mathcal{S}Pd(PPh_3)_3$ and $Pd(dba)(PPh_3)_2$ (Eqs. (3) and (4)) as in Scheme 1 ($L = PPh_3$). Indeed the kinetic law corresponding to the mechanistic Scheme 1 is logarithmic [88], as observed, with an apparent rate constant given by:

$$k_{app} = \frac{k}{1 + [dba]/K_1 + [PPh_3]/K_2}$$

or

$$\frac{1}{k_{app}[PPh_3]} = \left\{ \frac{1}{k[PPh_3]} + \frac{1}{kK_2} \right\} + \frac{[dba]}{kK_1[PPh_3]}$$

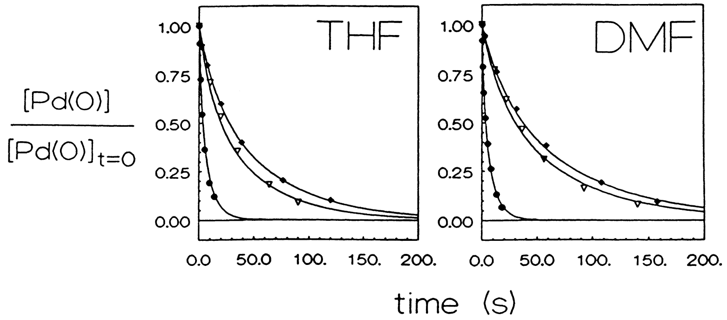


Fig. 6. Kinetics of the oxidative addition of PhI with $Pd(0)(PPh_3)_4$ (●) and with the palladium(0) complex generated *in situ* in the mixture of $Pd(dba)_2$ (2 mmol dm^{-3}) and 2 (▽), 4 (◆) equivalents of PPh_3, in THF and DMF (containing n-Bu_4NBF_4, 0.3 mol dm^{-3}), at 20 °C. The solid curves are the predicted variations simulated on the basis of the pertinent rate laws and rate constants [88].

which fits the experimental data (Fig. 5). The experimental intercept of the linear regression does not depend on $[PPh_3]$ which means that $1/k[PPh_3]$ is small compared to $1/kK_2$, so that kK_2 could be determined from the intercept. kK_1 was determined from the slope and K_0 from the ratio of these two values (Table 1) [88].

Determination of K_0 by three independent techniques results in similar values (Table 1). Whatever the solvent, the value of K_0 is less than unit which shows that for comparable dba and PPh_3 concentrations, the overall equilibrium (Eq. (5)) is in favor of $Pd(dba)(PPh_3)_2$ which is then the major complex in solution, whereas the concentration of the reactive species in the oxidative addition, $Pd(PPh_3)_2$, is considerably smaller. As a consequence of this interplay, when the reactivity of $Pd(PPh_3)_4$ was compared to that of mixtures of $Pd(dba)_2+n$L ($n=2$ or 4), the following order of reactivity was established (Fig. 6) [88]:

$$Pd(PPh_3)_4 > \{Pd(dba)_2+2PPh_3\} > \{Pd(dba)_2+4PPh_3\}$$

which shows that $\{Pd(dba)_2+2PPh_3\}$ is not equivalent to $Pd(PPh_3)_2$ and $\{Pd(dba)_2+4PPh_3\}$ is not equivalent to $Pd(PPh_3)_4$ as usually acknowledged. These kinetic data cast some light on many puzzling results reported in the literature [20,22,23,27,31].

2.2. Mixtures of $Pd(dba)_2+n(p\text{-}Z\text{-}C_6H_4)_3P$ ($n\geq 2$)

As for PPh_3, mixtures of $Pd(dba)_2$ and nL (L=*para*-Z-substituted triphenylphosphines, $n>2$) in DMF and THF, lead to the formation of $Pd(dba)L_2$ and PdL_3 in equilibrium with PdL_2 [90].

$$Pd(0)(dba)L_2+S \rightleftarrows SPd(0)L_2+\text{dba}\ K_1^Z \qquad (3')$$

$$SPd(0)L_3 \rightleftarrows SPd(0)L_2+L\ K_2^Z \qquad (4')$$

with the overall equilibrium:

$$S\mathrm{Pd(0)(dba)L_2} + \mathrm{L} \rightleftarrows S\mathrm{Pd(0)L_3} + \mathrm{dba} \quad K_0^Z = K_1^Z / K_2^Z \tag{5'}$$

For a given value of n, the equilibrium (Eq. (5′)) (constant K_0^Z) between $Pd(dba)L_2$ and PdL_3 lies more in favor of PdL_3 when the phosphine is less electron rich. The exchange of the dba ligand by a phosphine from $Pd(dba)L_2$ to form PdL_3 is then facilitated when the phosphine is less electron rich. In other words, the competition between dba and L to stabilize $Pd(0)L_2$ shifts in favor of L when the phosphine becomes less and less electron rich and the release of dba from $Pd(dba)L_2$ to form PdL_3 gets easier and easier.

Whatever the phosphine, the less ligated complex PdL_2 remains the reactive species in the oxidative addition with phenyl iodide.

$$S\mathrm{Pd(0)L_2} + \mathrm{PhI} \rightleftarrows \mathrm{PhPdIL_2} + S \quad k^Z \tag{6}$$

The kinetics of the oxidative addition with PhI was investigated as a function of the electron acceptor or donor properties of the phosphines. It is generally admitted that the oxidative addition is sensitive to electronic factors, the oxidative addition being faster when the phosphine is more electron rich. However, surprisingly, when the palladium(0) complex is generated from mixtures of $Pd(dba)_2$ and nL ($n \geq 2$), the oxidative addition does not follow a linear Hammett correlation. For $n=2$, 4 and 9, the plots of $\log(t_{1/2}^H / t_{1/2}^Z)$ (where $t_{1/2}^Z$ is the palladium(0) half life time at constant PhI concentration) versus the Hammett constant σ are not linear. Instead, bell shaped curves are obtained with a maximum whose value and position depends on n, i.e. on the phosphine concentration (Fig. 7) [90].

In fact, the overall reactivity in the oxidative addition is governed by two factors: (i) the intrinsic reactivity of PdL_2 in the oxidative addition expressed by k^Z in Eq. (6), and (ii) the concentration of PdL_2 which is controlled by the values of the equilibrium constants K_1^Z and K_0^Z. When the phosphine becomes more electron rich, the complex PdL_2 becomes more nucleophilic and k^Z increases. On the other hand,

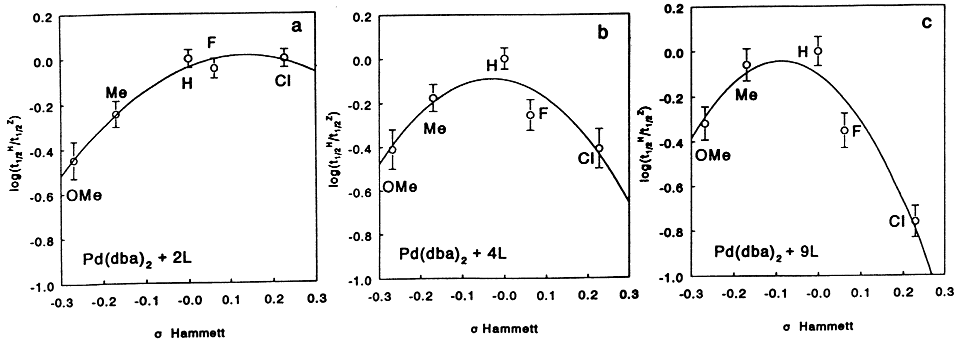


Fig. 7. Hammett plot for the oxidative addition of phenyl iodide with the palladium(0) generated in situ in mixtures of $Pd(dba)_2$ and n (p-Z-$C_6H_4)_3P$ in DMF at 20 °C. $[Pd(dba)_2] = 2\ \mathrm{mmol\ dm^{-3}}$; $[PhI] = 10\ \mathrm{mmol\ dm^{-3}}$. (a) $n=2$, (b) $n=4$, (c) $n=9$.

when the phosphine becomes more electron rich, the concentration of PdL_2 decreases because the equilibrium constants K_1^Z and K_0^Z decrease and the equilibria in Eqs. (3′) and (5′) shift more in favor of $Pd(dba)L_2$. Two antagonistic effects are involved. When the intrinsic reactivity of PdL_2 increases, its concentration decreases and the resulting effect is to afford bell shaped curves whose maximum value and position depend on *n*, the number of phosphine equivalents.

2.3. Mixtures of $Pd(dba)_2+n$TFP (TPF = tri-2-furylphosphine) ($n \geq 2$)

The tri-2-furylphosphine ligand TFP, has been recently introduced as ligand in palladium(0)-catalyzed reactions [39–48] and found to be very often more efficient than PPh_3. Reactivities of mixtures of $Pd(dba)_2+n$TFP have been compared to those of $Pd(dba)_2+nPPh_3$, as a function of *n*, in oxidative addition with phenyl iodide. The behavior of mixtures of $Pd(dba)_2+n$TFP obeys the general mechanism established for monodentate phosphines (Scheme 1). The determination of the equilibrium constant K_0 between $Pd(dba)(TFP)_2$ and $Pd(TFP)_3$ (Eq. (5)) shows that this equilibrium is less in favor of $Pd(dba)L_2$ than observed for PPh_3 (Table 2) [91]. This shows that the displacement of dba from the complex $Pd(dba)L_2$ to form L_3 is easier for TFP than for PPh_3. Since TPF is less basic than PPh_3, the effect of the basicity on the value of K_0 is consistent with that evidenced in the case of *para* substituted phosphines (see Section 2.2).

In DMF, the catalytic system $Pd(dba)_2+n$TFP was more reactive than $Pd(dba)_2+nPPh_3$ for any value of *n* ($n \geq 2$). In THF, the catalytic system $Pd(dba)_2+n$TFP was less reactive than $Pd(dba)_2+nPPh_3$ when $n=2$ or 4, whereas the reverse order of reactivity was observed for $n>6$ (Fig. 8) [91].

Thus, in THF, the order of reactivity strongly depends on the value of *n*. This behavior is rationalized as established above for *para* substituted phosphines, by the involvement of two antagonistic effects in the overall reactivity. When $n=2$, only equilibria in Eq. (3′) have to be considered. Since TFP is less basic than PPh_3, the intrinsic rate constant of the oxidative addition must respect the order: $k^{PPh3} > k^{TFP}$. Conversely, since $K_1^{PPh3} < K_1^{TFP}$, the concentration of $Pd(PPh_3)_2$ is less than that of $Pd(TFP)_2$. From these two antagonistic effects, PPh_3 results in a more reactive system than TFP with $k^{PPh3}K_1^{PPh3} > k^{TFP}K_1^{TFP}$ (Table 2) showing that k^{PPh3} is considerably higher than k^{TFP}.

Table 2
Determination of the equilibrium constants and kinetic parameters for palladium(0) complexes generated *in situ* in mixtures of $Pd(dba)_2^a$ and *n*L ($n>2$) and involved in the oxidative addition with PhI[a] according to Scheme 1, at 20 °C

Solvent	$10^2 \times kK_1$ (s^{-1})		K_0	
	PPh_3	TFP	PPh_3	TFP
DMF	0.63 ± 0.01	1.13 ± 0.01	0.14 ± 0.03	0.33 ± 0.05
THF	1.10 ± 0.01	1.07 ± 0.01	0.23 ± 0.03	0.26 ± 0.03

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

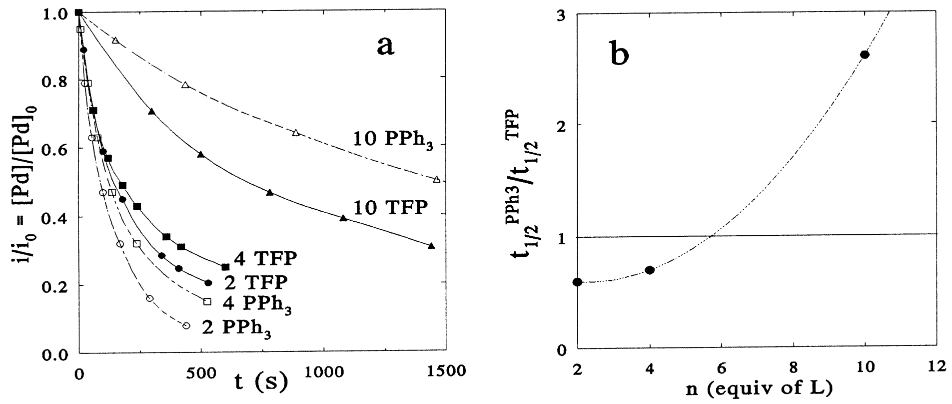


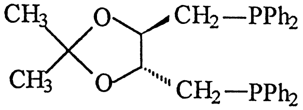
Fig. 8. Kinetics of the oxidative addition of PhI (2 mmol dm^{-3}) with the palladium(0) complex generated in situ from a mixture of Pd(dba)$_2$ (2 mmol dm^{-3})+nTFP (n=2, 4, 10) and from Pd(dba)$_2$ (2 mmol dm^{-3})+nPPh$_3$ (n=2, 4, 10 equiv.), monitored by cyclic voltammetry at a stationary gold disk electrode (0.5 mm diameter), with a scan rate of 0.2 V s^{-1}, in THF (containing n-Bu$_4$NBF$_4$, 0.3 mol dm^{-3}) at 20 °C. (a) Plot of $i/i_0 = [\mathrm{Pd}]/[\mathrm{Pd}]_0$ (i: oxidation peak current of Pd(0) at t, i_0: initial oxidation peak current of Pd(0)) as a function of time. (b) Plot of the ratio $t_{1/2}^{\mathrm{PPh3}}/t_{1/2}^{\mathrm{TFP}}$ as a function of n, in THF at 20 °C.

For higher values of n, ($n>2$) the equilibrium K_0 has also to be taken into consideration and experimentally: $K_0^{\mathrm{PPh3}} < K_0^{\mathrm{TFP}}$. Even if Pd(TFP)$_2$ is still intrinsically less reactive than Pd(PPh$_3$)$_2$, its concentration is considerably higher than that of Pd(PPh$_3$)$_2$ when n is large, resulting in a higher overall reactivity.

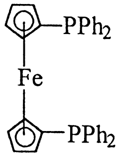
In practice, in THF, one uses catalytic systems Pd(dba)$_2$+nTFP in which n is small (n=2 or 4). From our results, one concludes that the use of TFP instead of PPh$_3$ results in slower oxidative additions. Under these conditions, the beneficial effect on catalytic reactions observed with TPF does not originate from the oxidative addition but certainly from a faster nucleophilic attack (or transmetallation) on the arylpalladium(II) complex formed in the oxidative addition, since these complexes are expected to be more electron deficient when ligated by TFP than by PPh$_3$. In such catalytic reactions, the oxidative addition should not then be the rate determining step of the catalytic cycle.

3. Mixtures of Pd(dba)$_2$ and bidentate phosphines (L–L)

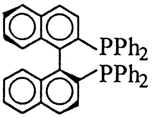
Chiral bidentate phosphine ligands such as DIOP [69–83] or BINAP [77–87] have been tested in palladium-catalyzed reactions. In order to characterize the crucial role of the ligand in asymmetric inductions, it is of interest to characterize the palladium(0) complex(es) active in oxidative additions, just in case this reaction could be responsible for the enantioselectivity. The oxidative addition of palladium(0) complexes generated in situ in mixtures of Pd(dba)$_2$ and bidentate phosphines was performed with PhI although the latter is not chiral. But as described above, this substrate allows an easy identification of the major complex in solution and the reactive species as well. Moreover, it allows a comparison of reactivities with monodentate phosphines.



DIOP



dppf



BINAP

3.1. *Mixtures of Pd(dba)$_2$+2 (L–L)*

Mixtures of $\mathrm{Pd(dba)_2+2(L\text{–}L)}$ (where L–L is a bidentate ligand such as dppm, dppe, dppp, dppb, dppf and DIOP) lead to the formation of $\mathrm{Pd(L\text{–}L)_2}$ complexes which do not undergo oxidative addition with phenyl iodide.

$$\mathrm{Pd(dba)_2+2(L\text{–}L)\rightarrow Pd(L\text{–}L)_2+2dba} \qquad (7)$$

$$\mathrm{Pd(L\text{–}L)_2+PhI}\nrightarrow\cdots$$

Surprisingly, a mixture of $\mathrm{Pd(dba)_2+2BINAP}$ does not afford $\mathrm{Pd(BINAP)_2}$ but instead Pd(dba)(BINAP) is formed and reacts with PhI [89].

$$\mathrm{Pd(dba)_2+2BINAP\rightarrow Pd(dba)(BINAP)+dba+BINAP} \qquad (8)$$

$$\mathrm{Pd(dba)(BINAP)+1BINAP}\nrightarrow\mathrm{Pd(BINAP)_2+dba} \qquad (9)$$

$$\mathrm{Pd(dba)(BINAP)+PhI\rightarrow PhPdI(BINAP)+dba} \qquad (10)$$

Thus, only mixtures of $\mathrm{Pd(dba)_2}$ with one equivalent of bidentate ligand L–L are of interest in terms of reactivity in oxidative addition with phenyl iodide [97].

3.2. *Mixtures of Pd(dba)$_2$+1 (L–L)*

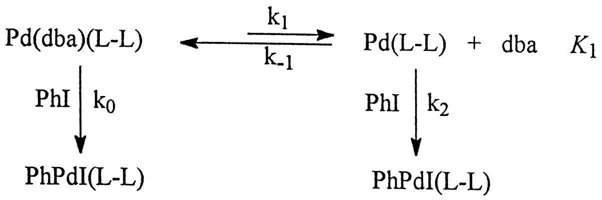
Mixtures of $\mathrm{Pd(dba)_2+1(L\text{–}L)}$ (L–L = dppm, dppe, dppp, dppb and DIOP) lead to Pd(dba)(L–L) complexes *via* the formation, with short times, of the complexes $\mathrm{Pd(L\text{–}L)_2}$ which then slowly con-proportionate with unreacted Pd(dba) to eventually generate Pd(dba)(L–L) [89,98]:

$$\mathrm{Pd(dba)_2\rightarrow Pd(dba)+dba} \qquad (1)$$

$$\mathrm{Pd(dba)+1L\text{–}L\rightarrow 1/2Pd(dba)+1/2Pd(L\text{–}L)_2+1/2dba}\ \text{fast} \qquad (11)$$

$$\mathrm{1/2Pd(dba)+1/2Pd(L\text{–}L)_2+1/2dba\rightarrow Pd(dba)(L\text{–}L)}\ \text{slow} \qquad (12)$$

When L–L = dppf and BINAP, the complex Pd(dba)(L–L) was directly observed

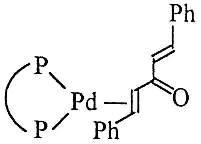


Scheme 2. Mechanism of the oxidative addition

without any hint of the intermediate formation of $Pd(L\text{–}L)_2$.

$$Pd(dba)_2 + 1(L\text{–}L) \rightarrow Pd(dba)(L\text{–}L) + dba \qquad (13)$$

The structure of complexes Pd(dba)(L–L) established by ^{31}P NMR spectroscopy for L–L = dppm [89], dppe [89,92], dppp [89,92], dppb [89], dppf [89], DIOP [89] and BINAP [89], or by X ray spectroscopy for L–L = dppe [92], obey the general formula:



Whatever the ligand, dppf, DIOP or BINAP, Pd(dba)(L–L) is the main complex in solution but is involved in an endergonic equilibrium (Eq. (14) in Scheme 2) with the less ligated complex Pd(L–L) and dba. The oxidative addition with phenyl iodide is slower in the presence of excess dba, showing that Pd(L–L) is the more reactive species. However, Pd(dba)(L–L) also reacts in parallel with phenyl iodide as summarized in Scheme 2 (the solvent is omitted for simplification) [89].

The reactivity of these different catalytic systems in the oxidative addition with phenyl iodide, could be compared on the basis of precise kinetic investigation. Thus, the following order of reactivity has been observed (Table 3) [89]:

$$\{Pd(dba)_2 + 1DIOP\} > \{Pd(dba)_2 + 1dppf\} \gg \{Pd(dba)_2 + 1BINAP\} \qquad (14)$$

Table 3
Comparative reactivity of palladium(0) complexes with PhI in THF, as a function of the ligand and the precursor

$[Pd(0)] = 2$ mmol dm^{-3}	T (°C)	[PhI] (mol dm^{-3})	$t_{1/2}$ (s)
$Pd(PPh_3)_4$	20	0.01	3.5
$Pd(dba)_2 + 2PPh_3$	20	0.01	20
$Pd(dba)_2 + 4PPh_3$	20	0.01	26
$Pd(dba)_2 + 1DIOP$	40	0.2	34
$Pd(dba)_2 + 1dppf$	40	0.2	110
$Pd(dba)_2 + 1BINAP$	40	0.2	16300

All these systems associated to one bidentate ligand are less reactive than $\{Pd(dba)_2+2PPh_3\}$ (Table 3).

Whereas in mixtures of $Pd(dba)_2$ and monodentate phosphine ligands, the single reactive species in the oxidative addition is PdL_2, two reactive species have been identified for bidentate ligands: Pd(L–L) and Pd(dba)(L–L). Since the spatial environment in Pd(dba)(L–L) differs from that of Pd(L–L), in the presence of a prochiral substrate, a possible asymmetric induction could differ from one complex to another. Moreover, the relative concentration of the two reactive palladium(0) complexes varies with the dba and $Pd(dba)_2$ concentration. Indeed, the concentration of dba increases with the concentration of $Pd(dba)_2$, with as a consequence a shift of the equilibrium (Eq. (14), Scheme 2) to the formation of Pd(dba)(L–L) and a decay of the concentration of the more reactive species Pd(L–L). Thus, the overall asymmetric induction might vary with the experimental conditions.

4. Conclusion

Whatever the phosphine ligand, monodentate (L) or bidentate (L–L), mixtures of $Pd(dba)_2$ and phosphines result in the formation of stable complexes $Pd(dba)L_2$ or Pd(dba)(L–L) which are the major complexes in solution. These complexes are involved in an equilibrium with dba and the less ligated complexes PdL_2 or Pd(L–L) which are the most reactive species in oxidative addition with phenyl iodide. Whereas $Pd(dba)L_2$ does not react in the oxidative addition, Pd(dba)(L–L) reacts with PhI albeit more slowly than Pd(L–L). Thus, the dba ligand plays a crucial role, since it is always involved in the major and less reactive complexes $Pd(dba)L_2$ or Pd(dba)(L–L) and thus controls the availability of the most reactive species. Indeed, the presence of these stable and major complexes diminishes the concentration of the more reactive species PdL_2 or Pd(L–L) and consequently controls the rate of the overall reaction. The overall reactivity is governed both by the intrinsic reactivity of the reactive species (mainly controlled by electronic factors: the basicity of the phosphine for comparable cone angles) and its concentration (in the equilibrium with the major complex, controlled by electronic and steric factors). These two parameters have antagonistic effects and as a result, non-linear Hammett correlation is observed in the oxidative addition versus the basicity of the phosphine, for monodentate ligands. In conclusion, dba in not a labile and passive ligand as usually considered.

Acknowledgements

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[97] Although Pd(L–L)$_2$ complexes do not react with PhI, they can activate other organic substrates such as allylic acetates [4,9,10].
[98] See Refs. [14,16] in Ref. [89] of this paper.