Kinetics of the Oxidative Addition of *ortho*-Substituted Aryl Halides to Palladium(0) Complexes

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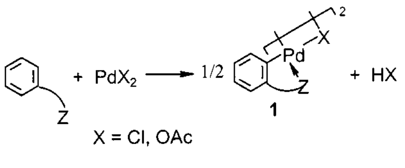
The rate constant of the oxidative addition of *ortho*-substituted aryl halides, *o*-$ZCH_2–C_6H_4–X$ [X = I, Br; Z = OMe, NEt_2, $N(CH_2)_5$] to $Pd^0(PPh_3)_4$ or to Pd^0(dba)(dppp) generated from $Pd^0(dba)_2$ and 1 equiv. of dppp is determined. The oxidative addition is slower for *ortho*-substituted aryl halides than for the corresponding nonsubstituted or *meta*-substituted aryl halides. The *ortho* substituents investigated here do not participate in the oxidative addition by a preliminary complexation of the active $Pd^0(PPh_3)_2$ or Pd^0(dppp) complex. The observed decelerating effect induced by the *ortho* substituents is due to steric hindrance and electronic donor effects and is less important for aryl bromides than for aryl iodides; *ortho*-substituted aryl iodides remain more reactive than *ortho*-substituted aryl bromides for both ligands PPh_3 and dppp. The *cis*-(*o*-$ZCH_2–C_6H_4$)PdX(dppp) complexes are formed in the oxidative addition whereas an equilibrium takes place between *trans*-(*o*-$ZCH_2–C_6H_4$)$PdX(PPh_3)_2$ and (*o*-$ZCH_2–C_6H_4$)$PdX(PPh_3)$(Z–*Pd*) complexes.

Introduction

Dimeric *ortho*-palladated complexes **1** are synthesized by reaction of a Pd^{II} salt and a substituted arene, in which the substituent may be a ligand for the Pd^{II} centers [Equation (1)].[1–7] This reaction is regarded as a preliminary complexation of the Pd^{II} salt by the substituent of the arene, followed by an intramolecular electrophilic aromatic substitution of the Pd^{II} center.[8] When the coordinated atom Z (Z = N, O) is linked to the arene through one atom (C or N) the resulting five-membered palladated complexes **1** are quite stable.[1–7] Monomeric complexes **2** and **3** are generated from dimeric complexes **1** by addition of 1 or 2 equiv. of L per Pd, respectively [Equation (2)];[9,10] *ortho*-palladated complexes **1** are also generated by an oxidative addition of an *ortho*-substituted aryl halide to a Pd^0 complex, $Pd^0(dba)_2$ [Equation (3)], with subsequent formation of complexes **2** and **3** after addition of a ligand [Equation (2)].[9–10]



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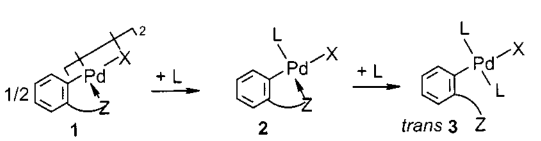

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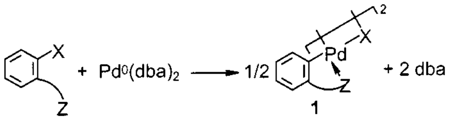

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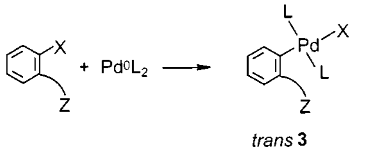
A recent paper[11] reports the synthesis of phosphane-bis(ligated) complexes **3** by oxidative addition of aryl bromides, substituted in the *ortho* position by CHO or C(O)Me, to Pd^0 complexes ligated by PPh_3 [Equation (4)]. Phosphane-monoligated complexes **2** are formed in the case of a bulky ligand L = P(*o*-tolyl)$_3$ and a C(O)Me substituent, which is able to coordinate the Pd^{II} center by the O atom.



(4)

Whereas reactions of *ortho*-substituted aryl halides with nucleophiles (alkynes,[12,13] alkenes,[13,14] organometallic reagents[6,15]) are catalyzed by Pd^0 complexes, reactions involving substituted arenes cannot be catalyzed by Pd^{II} complexes able to activate the initial substituted arene, unless the Pd^0 complex generated in the last step[4,7,16] is oxidized back to a Pd^{II} complex. To the best of our knowledge, the recycling of the Pd^{II} catalyst by oxidation has not yet been realized.[7]

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Pd^0-catalyzed cross-coupling reactions of nucleophiles with *ortho*-substituted aryl halides are usually slower than with the corresponding nonsubstituted or *para*/*meta*-substituted aryl halides.[6,15] The three main steps involved in the catalytic cycle (oxidative addition, transmetallation, and reductive elimination) may be affected by the *ortho* substitution of the aryl derivatives,[15] due to steric hindrance around the metal center and to electronic effects consecutive to potential intramolecular complexation of the substituent for the metal centers. Nonsubstituted or *para*/*meta*-substituted aryl iodides are usually more reactive than the corresponding aryl bromides.[6,15] This is rationalized by considering that the oxidative addition becomes rate-determining when considering aryl bromides, which indeed are less reactive with Pd^0 complexes than aryl iodides in oxidative additions.[17,18] In the case of *ortho*-substituted aryl halides, the situation is much more complex in the sense that the *ortho* substituent may induce a steric hindrance, which is expected to slow down the oxidative addition. However, *ortho*-substituted aryl bromides become globally less bulky than *ortho*-substituted aryl iodides due to the smaller size of the Br atom compared to that of the I atom. On the other hand, the Pd^0L_2 (L = phosphane) complex, active in the oxidative addition step, is usually present at low concentration because it is involved in an endergonic equilibrium with a major but unreactive Pd^0L_2L' complex (L = phosphane, L′ = phosphane[19] or dba[20]). A preliminary complexation of the active Pd^0L_2 complex by the *ortho* substituents of the aryl halides should result in an intramolecular oxidative addition step with a consequently faster overall reaction.

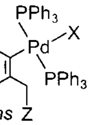
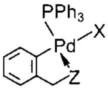
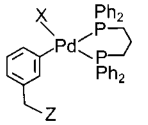
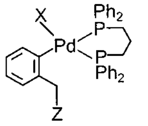
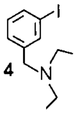
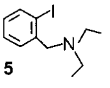
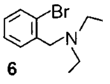
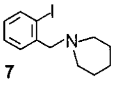
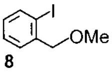
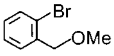
These antagonist effects prompted us to investigate the kinetics of the oxidative addition of *ortho*-substituted aryl iodides and bromides with Pd^0 complexes ligated by a monodentate ligand as in $Pd^0(PPh_3)_4$ or by a bidentate ligand as in Pd^0(dba)(dppp). The latter was generated by treating $Pd^0(dba)_2$ with 1 equiv. of dppp [dppp = $Ph_2P-(CH_2)_3-PPh_2$].[21,22] The *ortho* substituents are either $-CH_2-NR_2$ or $-CH_2-OR$ groups so that potentially five-membered palladated complexes might be generated.

Results and Discussion

Characterization of the (Aryl)palladium(II) Complexes Formed in the Oxidative Addition of *ortho*-Substituted Aryl Iodides and Bromides to Palladium(0) Complexes

Before discussing kinetic data on the comparative reactivity of *ortho*-substituted aryl iodides and bromides with Pd^0 complexes, the (aryl)palladium(II) complexes formed in the

Table 1. (Aryl)palladium(II) complexes generated in the oxidative addition of ArX (X = I, Br) to $Pd(PPh_3)_4$ or to $\{Pd(dba)_2$ + 1 equiv. dppp} in toluene

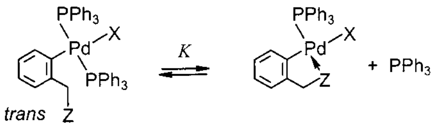
Entry	ArX	$ArPdI(PPh_3)_2$ *trans* δ_P, ppm [a]	 *trans* δ_P, ppm [a]	 δ_P, ppm [a]	ArPdI(dppp) *cis* δ_P, ppm [a]	 δ_P, ppm [a]	 δ_P, ppm [a]
1	PhI	22.9 (s)			−8.0 (d, *J* = 53Hz)[b] 13.1 (d, *J* = 53Hz)[b]		
2	 **4**	22.7 (s) *m*–**4a**				−10.3 (d, *J* = 52Hz) 10.9 (d, *J* = 52Hz) *m*–**4c**	
3	 **5**		22.6 (s) **5a**	41.1 (s)[c] **5b** [traces][d]			−9.4 (d, *J* = 54 Hz) 9.4 (d, *J* = 54 Hz) **5c**
4	 **6**		22.0 (s) **6a**	41.6 (s)[c] **6b** [traces][d]			–
5	 **7**		21.7 (s) **7a** [33 %][e]	41.7 (s)[e] **7b** [31 %][d,e]			–
6	 **8**		22.2 (s) **8a**	n.o.[f] **8b**			−10.4 (d, *J* = 57Hz) 9.3 (d, *J* = 57Hz) **8c**
7	 **9**		22.2 (s) **9a**	n.o.[f] **9b**			−9.6 (d, *J* = 51Hz) 12.3 (d, *J* = 51Hz) **9c**

[a] Determined in [D$_1$]chloroform vs. H_3PO_4 as an external standard at 293 K. – [b] *cis*-PhPdI(dppp).[36] – [c] A minor singlet for PPh_3 at δ = −5.1 was also observed. – [d] Data in square brackets are indicative of the relative integration of the ^{31}P NMR signals. – [e] A broad singlet for PPh_3 at δ = −5.2 was also observed, integrating for 32%. – [f] n.o.: not observed.

oxidative addition were first characterized. The reactions were performed by treating the aryl halides (in large excess) with either $Pd^0(PPh_3)_4$ or with a mixture $Pd^0(dba)_2$ + 1 equiv. of dppp in toluene. The complexes were isolated and characterized by ^{31}P NMR spectroscopy (Table 1).

The oxidative addition of PhI or the *meta*-substituted aryl iodide **4** to $Pd^0(PPh_3)_4$ gave the expected *trans*-$PhPdI(PPh_3)_2$ and *meta*-**4a** complexes, respectively as unique complexes. (Table 1, Entries 1,2). The *ortho*-substituted aryl iodide **5** and bromide **6** gave a major complex **5a** and **6a**, respectively, characterized by a narrow singlet at $\delta \approx 22$ in the ^{31}P NMR spectra (Table 1, Entries 3,4), which is indicative of two equivalent PPh_3 moieties ligated to the Pd^{II} center.[11] The two PPh_3 groups are in a *trans* position, in agreement with the recently published X-ray structure of a related complex with X = Br and CHO as the *ortho* substituent.[11] The complex is slightly distorted square-planar. The two triphenylphosphane ligands ($\delta = 23.2$) are in a *trans* position, and are magnetically equivalent because the plane of the *ortho*-substituted aryl group is perpendicular to the plane of P, Pd, P, and Br.

In both cases, besides a minor signal for PPh_3 at $\delta = -5$, another minor narrow singlet was detected at $\delta \approx 41$ and assigned to complexes **5b** and **6b** (Table 1). In these complexes the Pd^{II} center is ligated by only one PPh_3, the fourth coordination site being occupied by the amine substituent. Indeed, the singlets at $\delta = 41.1$ and 41.7 disappeared after addition of PPh_3, which is evidence of an equilibrium between the complexes **5a/5b** or **6a/6b** and PPh_3 [Equation (5)]. Moreover, the values of $\delta = 41.1$ and 41.6 assigned to **5b** and **6b**, respectively, are very similar to those reported for related cyclopalladated complexes where the Pd^{II} center is ligated by only one PPh_3.[11,23]



(5)

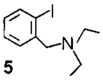
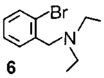
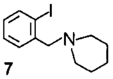
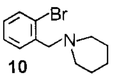
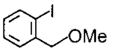
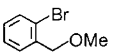
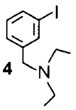
This is also in agreement with literature results, which report that phosphane-bis(ligated) (aryl)palladium(II) complexes are formed after addition of a second ligand to phosphane-monoligated complexes [Equation (2)].[9,10]

Stronger evidence for the equilibrium [Equation (5)] was provided upon treating the aryl iodide **7** with $Pd^0(PPh_3)_4$. Indeed, three broad signals ($\Delta\nu_{1/2}$ = 152 Hz) of very similar integration were observed in the ^{31}P NMR spectrum at δ = 41.7, 21.7, and −5.2, and these were assigned to complexes **7b**, **7a**, and PPh_3, respectively (Table 1, Entry 5). Addition of PPh_3 shifted the equilibrium [Equation (5)] towards its left-hand side, and complex **7a** was then observed as the major complex. The equilibrium constant *K* between **7a**, **7b**, and PPh_3 [Equation (5)] was estimated from the ^{31}P NMR spectroscopic data to $K/c_0 = 0.6$ (in $CDCl_3$ at 25 °C for $c_0 \approx 20$ mM). The oxidative addition of aryl halides **8** or **9**, substituted in *ortho* position by a $-CH_2-OMe$ group, to $Pd^0(PPh_3)_4$ generated the phosphane-bis(ligated) complexes **8a** or **9a**, respectively (Table 1, Entries 6,7).

The oxidative addition of *ortho*-substituted aryl iodides or bromides to the Pd^0 complex generated from $Pd^0(dba)_2$ + 1 equiv. of dppp always gave the corresponding *cis*-ArPdX(dppp) complexes without any intramolecular coordination by the *ortho* substituent (Table 1, last column). In all cases, the ^{31}P NMR spectrum exhibited two doublets caused by the coupling of two nonequivalent P atoms ligated to the Pd^{II} center in a *cis* position. Moreover, the observed chemical shifts were very similar to those of the complexes generated by oxidative addition of PhI or *meta*-substituted phenyl iodide **4** (Table 1, Entries 1 and 2, last column), in which no internal coordination by the substituent may occur, by construction.

Therefore, in almost every case, the oxidative addition generates a major *trans*-(aryl)palladium(II) complex ligated by two phosphane ligands, without any intramolecular coordination of the *ortho* substituent. It is only with a monophosphane ligand (PPh_3) that an intramolecular complexation of the substituent may occur (Table 2, Entry 5),

Table 2. Comparative reactivity of ArX (X = I, Br) in their oxidative addition to $Pd^0(PPh_3)_4$ and to [$Pd^0(dba)_2$ + 1 equiv. of dppp] in DMF

Entry	ArX	T (°C)	$Pd^0(PPh_3)_4$	$Pd^0(dba)_2$ + 1 dppp
			k_{app} (M^{-1} s^{-1})	k_{app} (M^{-1} s^{-1})
1	PhI	25	25	–
2	PhI	40	–	1.9×10^{-3}
3	PhBr	25	1.5×10^{-3}	–
4	PhBr	40	10^{-2}	1.7×10^{-4}
5	 **5**	25	7.0	–
6	**5**	40	–	1.4×10^{-3}
7	 **6**	40	3.2×10^{-3}	–
8	 **7**	25	0.8	–
9	**7**	40	–	1.4×10^{-3}
10	 **10**	40	3.6×10^{-3}	–
11	 **8**	25	1.8	–
12	**8**	40	–	8.5×10^{-4}
13	 **9**	40	2.6×10^{-3}	–
14	 **4**	25	29	–

involving decomplexation of one PPh_3 through an endergonic equilibrium [Equation (5)]. This does not occur with the bidentate ligand dppp considered here because the decomplexation of one phosphorus atom of a bidentate P,P ligand possessing a small bite angle is not favored.[24]

Comparative Reactivity of *ortho*-Substituted Aryl Iodides and Bromides in Their Oxidative Addition to Palladium(0) Complexes in DMF

Oxidative Addition to $Pd^0(PPh_3)_4$

The mechanism of the oxidative addition of aryl halides to $Pd^0(PPh_3)_4$ is now well established and proceeds according to Scheme 1 (S = solvent).[19,25] The kinetics of the oxidative addition was monitored by amperometry performed at a rotating disk electrode, polarized at +0.3 V vs. SCE, on the plateau of the oxidation wave of $Pd^0(PPh_3)_3$ (c_0 = 2 mM in DMF containing $n\mathrm{Bu_4NBF_4}$, 0.3 M). The decay of the oxidation current intensity, proportional to the Pd^0 concentration, was recorded versus time, after addition of the aryl halide in excess.[25]

$$Pd^0(PPh_3)_4 \rightleftarrows Pd^0(PPh_3)_3 + PPh_3$$
$$Pd^0(PPh_3)_3 \xrightleftharpoons{K_0} SPd^0(PPh_3)_2 + PPh_3$$
$$SPd^0(PPh_3)_2 + ArX \xrightarrow{k} ArPdX(PPh_3)_2$$

Overall reaction:

$$Pd^0(PPh_3)_4 + ArX \xrightarrow{k_{app}} ArPdX(PPh_3)_2 + 2PPh_3 \qquad (6)$$

Scheme 1. Mechanism of the oxidative addition of aryl halides to $Pd^0(PPh_3)_4$; S = solvent

The plot of $2\ln(i/i_0) + 1 - i/i_0 = 2\ln([Pd^0]/[Pd^0]_0) + 1 - [Pd^0]/[Pd^0]_0$ versus time was linear (Figure 1) (i: oxidation current intensity at t; i_0: initial oxidation current intensity).

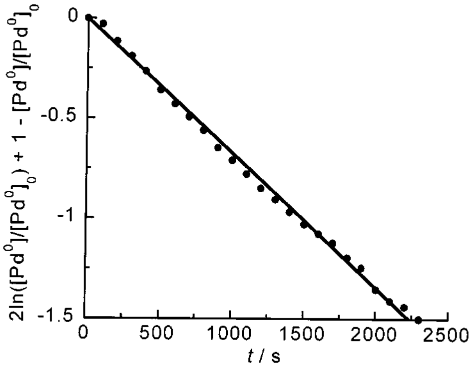


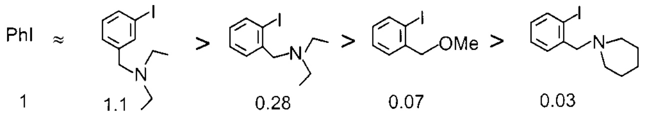
Figure 1. Oxidative addition of the aryl bromide **6** [0.2 M in DMF containing $n\mathrm{Bu_4NBF_4}$ 0.3 M)] to $Pd^0(PPh_3)_4$ (2 mM) at 40 °C, monitored by amperometry at a rotating gold disk electrode (i.d. 2 mm, ω = 105 rad·s^{-1}) polarized at + 0.35 V; plot of $2\ln(i/i_0) + 1 - i/i_0 = 2\ln([Pd^0]/[Pd^0]_0) + 1 - [Pd^0]/[Pd^0]_0$ versus time (i: oxidation current intensity at t; i_0: initial oxidation current intensity) [see Equation (7)]

Note that the kinetic law [Equation (7)] is not strictly logarithmic due to the PPh_3 release during the reaction (Scheme 1).[25]

$$2\ln([Pd^0]/[Pd^0]_0) + 1 - [Pd^0]/[Pd^0]_0 = -kK_0[ArX]t/c_0 = -k_{app}[ArX]t \qquad (7)$$

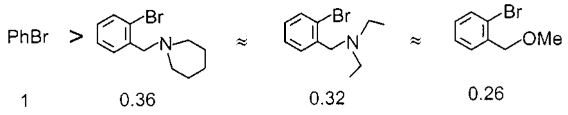
The apparent rate constant k_{app} of the overall oxidative addition [Equation (6)] was determined from the slope of the regression lines [Equation (7), Figure 1]. From the results gathered in Table 2, one observes the following order of reactivity: ArI >> ArBr, for identical *ortho* substituents, even when considering that the experimental temperature was generally lower for ArI (25 °C) than for ArBr (40 °C). This is consistent with the higher reactivity of nonsubstituted (Table 2, Entries 1−4) or *para*/*meta*-substituted aryl iodides when compared to the related aryl bromides as observed by Fitton and Rick.[17]

In the aryl iodides series (Scheme 2), the *meta* substitution does not significantly affect the rate of the oxidative addition. This rules out a preliminary complexation of the active $Pd^0(PPh_3)_2$ by the substituent, which would have affected the rate of the oxidative addition by decreasing the active $Pd^0(PPh_3)_2$ concentration. The *ortho* substitution slows down the oxidative addition. Since no precomplexation of the $Pd^0(PPh_3)_2$ complex by the *ortho* substituent occurs before the oxidative addition step, the mechanism of the oxidative addition (Scheme 1) is still valid. The decelerating effect is then rationalized by the cumulative influence of steric hindrance and electron-donating property of the substituent efficient in the *ortho* position, which both decrease the reaction rate. Electron-donating groups are indeed known to slow down oxidative additions of aryl derivatives to $Pd^0(PPh_3)_4$ complexes.[17−19] However, although the $-CH_2-OMe$ substituent is less electron-donating and less bulky than $-CH_2-NEt_2$, the corresponding aryl iodide is significantly less reactive, a fact which is difficult to rationalize. Some stabilization may occur in the transition state en route to the Pd^{II} center.



Scheme 2. Relative reactivity of aryl iodides in their oxidative addition to $Pd^0(PPh_3)_4$ at 25 °C

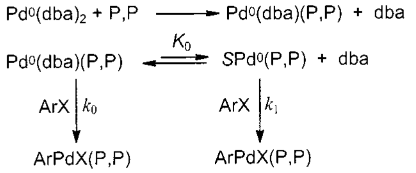
In the aryl bromides series (Scheme 3), the decelerating effect of the *ortho* substituent is less important than the corresponding one in the aryl iodide series (Scheme 2). This is consistent with the smaller size of the Br atom compared to that of the I atom, which globally decreases the steric constraint imposed by an *ortho* substituent in the aryl bromide compared to that in the corresponding aryl iodide.



Scheme 3. Relative reactivity of aryl bromides in their oxidative addition to $Pd^0(PPh_3)_4$ at 40 °C

Oxidative Addition to $Pd^0(dba)_2$ + 1 equiv. of dppp

As already reported, a major complex $Pd^0(dba)(P,P)$ is formed from $Pd^0(dba)_2$ and 1 equiv. of bidentate P,P ligands.[21,22] The mechanism of the oxidative addition of aryl halides has been established for P,P ligands (Scheme 4). The most reactive complex is the minor complex $SPd^0(P,P)$ but the major complex $Pd^0(dba)(P,P)$ is also reactive ($k_1 > k_0$).[22]



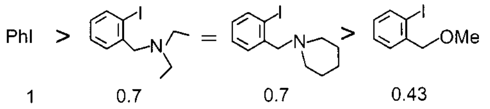
Scheme 4. Mechanism of the oxidative addition of aryl halides to the Pd^0 complexes generated from $Pd^0(dba)_2$ and 1 equiv. of bidentate P,P ligand.

In DMF, the formation of the major complex $Pd^0(dba)(dppp)$ from $Pd^0(dba)_2$ and 1 equiv. of dppp is a slow reaction because of the formation of the intermediate complex $Pd^0(dppp)_2$.[22] Therefore, the reactivity of aryl iodides or bromides in oxidative addition to $Pd^0(dba)(dppp)$ was investigated at least 90 min after mixing $Pd^0(dba)_2$ (2 mM in DMF) and dppp (2 mM) at room temperature, to ensure the total formation of $Pd^0(dba)(dppp)$. The apparent rate constant k_{app} of the overall oxidative addition [Equation (8)] was determined as explained above for $Pd^0(PPh_3)_4$, except that the rotating disk electrode was polarized at +0.7 V vs. SCE because $Pd^0(dba)(dppp)$ is less easily oxidized than $Pd^0(PPh_3)_3$.

$$Pd^0(dba)(dppp) + ArX \xrightarrow{k_{app}} ArPdX(dppp) + dba \qquad (8)$$

The reactions were considerably slower compared to that of $Pd^0(PPh_3)_4$. They were then performed at 40 °C even for aryl iodides (Table 2). It has already been observed that $Pd^0(PPh_3)_4$ is generally considerably more reactive than $Pd^0(dba)_2$ + 1 equiv. of P,P,[20,22] despite the fact that P,P ligands are usually more basic and possess a smaller P−Pd−P angle than PPh_3. This arises from the fact that the concentration of $SPd^0(PPh_3)_2$ in the equilibrium with $Pd^0(PPh_3)_3$ (Scheme 1) is higher than that of $SPd^0(P,P)$ in the equilibrium with $Pd^0(dba)(P,P)$ (Scheme 4).[20]

As observed above for $Pd^0(PPh_3)_4$, PhI is more reactive than PhBr (Table 2, Entries 2, 4). The kinetics of the oxidative addition was only investigated for *ortho*-substituted aryl iodides, because reactions with *ortho*-substituted aryl bromides were too slow, even in the presence of ArBr in very large excess. The concomitant decomposition of the Pd^0 complex could not be excluded. In the aryl iodides series (Scheme 5), the *ortho* substitution slows down the oxidative addition, but the decelerating effect is less important than that observed with $Pd^0(PPh_3)_4$ (Scheme 2).



Scheme 5. Relative reactivity of aryl iodides in their oxidative addition to the Pd^0 complexes generated in the mixture $Pd^0(dba)_2$ and dppp at 40 °C

Conclusion

Determination of the rate constant of the oxidative addition of *ortho*-substituted aryl halides o-$ZCH_2-C_6H_4-X$ [X = I, Br; Z = OMe, NEt_2, $N(CH_2)_5$] with $Pd^0(PPh_3)_4$ or with the Pd^0 complexes generated from $Pd^0(dba)_2$ and 1 equiv. of dppp shows that the oxidative addition is slower for *ortho*-substituted aryl halides than for the corresponding nonsubstituted or *meta*-substituted aryl halides. This means that the *ortho* substituents do not participate in the oxidative addition by a preliminary complexation of the active $Pd^0(PPh_3)_2$ or $Pd^0(dppp)$ complex. Oxygen and nitrogen ligands are indeed poor ligands for Pd^0 centers, unless they are involved in a bidentate complexation as for P,O or P,N ligands.[26] The observed decelerating effect induced by the *ortho* substituent is due to steric hindrance and electronic effects caused by the electron-donor properties of the substituents. These effects are less important for *ortho*-substituted aryl bromides than for *ortho*-substituted aryl iodides. Considering the same substituent, *ortho*-substituted aryl iodides remain more reactive than *ortho*-substituted aryl bromides, whatever the ligand. No inversion of reactivity occurs in the oxidative addition due to the *ortho* substitution. Were an inversion of reactivity observed in a Pd-catalyzed cross-coupling reaction, it should then arise at the level of the transmetallation step, which follows the oxidative addition. This probably lies at the origin of the inversion of reactivity observed in the palladium-catalyzed coupling of organomanganese derivatives with aryl halides, for which *ortho*-substituted aryl iodides were found to be less reactive than *ortho*-substituted aryl bromides.[27]

In this respect, it is worth to emphasize that an equilibrium results between *trans*-(o-$ZCH_2-C_6H_4$)$PdX(PPh_3)_2$ complexes formed in the oxidative addition and (o-$ZCH_2-C_6H_4$)$PdX(PPh_3)$(*Z−Pd*) exhibiting an intramolecular complexation of the *ortho* substituent. Nitrogen ligands are indeed good ligands for Pd^{II} centers, and the intramolecular character of the complexation enhances this effect. The latter complex might be involved in reactions with nucleophiles (transmetallation step). The *cis*-(o-$ZCH_2-C_6H_4$)$PdX(dppp)$ complexes are formed when the Pd^0 is ligated by a bidentate ligand such as dppp. The bidentate character of this P,P ligand with a small bite angle makes the intramolecular complexation by the *ortho* substituent less probable.

Experimental Section

General: All experiments were performed using standard Schlenk techniques under argon. − DMF was distilled from calcium hydride under vacuum. Toluene was distilled from sodium. − Iodo- and bromobenzene were commercial (Acros) and used after filtration through alumina. The dppp was commercial (Aldrich) and used without purification. $Pd(PPh_3)_4$,[28] $Pd(dba)_2$,[29] and $PhPdI(PPh_3)_2$ [17] were synthesized according to published procedures, as well as compounds **5**,[30,31] **6**,[32] **7**,[31] **8**,[33] **9**,[34] and **10**.[32] − ^{31}P NMR spectra were recorded with a Bruker spectrometer (162 MHz) using H_3PO_4 as an external reference, ^1H NMR spectra with a Bruker spectrometer (250 MHz) using TMS as an internal reference.

Diethyl(3-iodobenzyl)amine (4): Synthesis according to a published procedure[32] by treating 3-iodobenzyl bromide with diethylamine in anhydrous diethyl ether at room temperature. − ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.86$ (t, $J = 7.0$ Hz, 6 H, CH_3), 2.33 (q, $J = 7.0$ Hz, 4 H, $CH_2{-}CH_3$), 3.31 (s, 2 H, $CH_2{-}N$), 6.83 (t, $J = 7.7$ Hz, 1 H, 5-*H*), 7.13 (d, $J = 7.7$ Hz, 1 H, 6-*H*), 7.37 (d, $J = 7.7$ Hz, 1 H, 4-*H*), 7.57 (s, 1 H, 2-*H*).

General Procedure for the Oxidative Addition: Complexes *m*-**4a**, **5a**, **6a**, **7a**, **8a**, and **9a** were synthesized according to a Fitton procedure.[17] In a Schlenk flask containing a solution of the aryl halide (from $4{\cdot}10^{-3}$ mol for the aryl iodides **4**, **5**, **7**, and **8** to 0.05 mol for the aryl bromides **6** and **9**) in 5 mL of degassed toluene was added 0.58 g ($0.5{\cdot}10^{-3}$ mol) of $Pd(PPh_3)_4$. The solution was kept overnight at room temperature for aryl iodides and heated during 4 h for aryl bromides. After filtration, the toluene was removed under vacuum, and the crude mixture was triturated with diethyl ether to eliminate the excess phosphane and aryl halide. The solid complexes were then characterized by ^{31}P NMR spectroscopy (Table 1).

(o-$CH_3OCH_2{-}C_6H_4$)$PdI(PPh_3)_2$ (8a): ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.85$ (s, 3 H, OCH_3), 4.14 (s, 2 H, CH_2), 6.18 (t, $J = 7.0$ Hz, 1 H, 5-*H*), 6.35 (d, $J = 7.0$ Hz, 1 H, 3-*H*), 6.45 (t, $J = 7.0$ Hz, 1 H, 4-*H*), 6.74 (d, $J = 7.0$ Hz, 1 H, 6-*H*), 7.1−7.4 (m, 30 H, *H* of PPh_3).

Complexes *m*-**4c**, **5c**, **8c**, and **9c** were synthesized according to an adapted version of the Herrmann procedure.[35] In a Schlenk flask, containing a solution of 0.28 g ($0.5{\cdot}10^{-3}$ mol) of $Pd(dba)_2$ in 5 mL of degassed toluene, was added 0.21 g ($0.5{\cdot}10^{-3}$ mol) of dppp. After 2 h, 0.05 mol of the aryl halide was added. The solution was heated during 4 h for aryl iodides **4**, **5**, **8** and 6 h for the aryl bromide **9**. After filtration, the toluene was removed under vacuum, and the crude mixture was triturated with diethyl ether to eliminate the excess aryl halide. The pale-yellow complexes were then crystallized from chloroform/petroleum ether and characterized by ^{31}P NMR spectroscopy (Table 1).

Electrochemical Set-up for Amperometry and Kinetic Measurements of the Oxidative Addition: Electrochemical experiments were carried out in a three-electrode cell connected to a Schlenk line. The cell was equipped with a double envelope to maintain a constant temperature (Lauda RC20 thermostat). The working electrode consisted of a gold disk (i.d. 2 mm, Tacussel EDI 65109). 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 $n\mathrm{Bu_4NBF_4}$ (0.3 mol dm^{-3}) in 3 mL of DMF. 15 mL of DMF containing the same concentration of supporting electrolyte was poured into the cell followed by 34 mg ($0.03{\cdot}10^{-3}$ mol) of $Pd(PPh_3)_4$. The kinetic measurements were performed using the rotating gold disk electrode with an angular velocity of 105 rad s^{-1} (Tacussel controvit). The potential of the rotating disk electrode was set at +0.35 V on the oxidation plateau wave of $Pd^0(PPh_3)_4$. The suitable amount of the aryl halide was added and the decay of the oxidation current was then monitored as a function of time. − In other experiments, 17 mg ($0.03{\cdot}10^{-3}$ mol) of $Pd(dba)_2$ was added, followed by 12 mg ($0.03{\cdot}10^{-3}$ mol) of dppp. After 2 h, the potential of the rotating disk electrode was set at +0.70 V on the oxidation plateau wave of $Pd^0(dba)(dppp)$. The decay of the oxidation current was monitored as a function of time after addition of the suitable amount of the aryl halide.

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[1] J. Dehand, M. Pfeffer, *Coord. Chem. Rev.* **1976**, *18*, 327−352.
[2] M. I. Bruce, *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 76−86.
[3] I. Omae, *Chem. Rev.* **1979**, *79*, 287−321.
[4] A. D. Rybov, *Synthesis* **1985**, 233−252.
[5] G. R. Newkome, W. E. Puckatt, V. K. Gupta, G. E. Kiefer, *Chem. Rev.* **1986**, *86*, 451−489.
[6] S. Tsuji, *Palladium Reagents and Catalysis*, John Wiley & Sons, Chichester, **1995**.
[7] M. Pfeffer, *Pure & Appl. Chem.* **1992**, *64*, 335−342.
[8] A. C. Cope, E. C. Friedrich, *J. Am. Chem. Soc.* **1968**, *90*, 909−913.
[9] P. W. Clark, S. F. Dyke, *J. Organomet. Chem.* **1983**, *259*, C17−C19.
[10] P. W. Clark, S. F. Dyke, *J. Organomet. Chem.* **1985**, *281*, 389−396.
[11] J. Vicente, J.-A. Abad, E. Martinez-Viviente, M. C. Ramirez de Arellano, *Organometallics* **2000**, *19*, 752−760.
[12] N. Beydoum, M. Pfeffer, *Synthesis* **1990**, 729−731.
[13] B. J. Soderberg, "Transition Metal Alkyl Complexes: Oxidative Addition and Insertion" in *Comprehensive Organometallic Chemistry II*, Elsevier, Oxford, New York, Tokyo, **1995**, vol. *12*, p. 241−299.
[14] R. C. Larock, N. Berrios-Peña, K. Narayanan, *J. Org. Chem.* **1990**, *55*, 3447−3450.
[15] V. Farina, "Transition Metal Alkyl Complexes: Oxidative Addition and Transmetallation" in *Comprehensive Organometallic Chemistry II*, Elsevier, Oxford, New York, Tokyo, **1995**, vol. *12*, p. 161−240.
[16] F. Maassanari, M. Pfeffer, G. Le Borgne, *Organometallics* **1987**, *6*, 2029−2043.
[17] P. Fitton, E. A. Rick, *J. Organomet. Chem.* **1971**, *28*, 287−291.
[18] A. Jutand, A. Mosleh, *Organometallics* **1995**, *14*, 1810−1817.
[19] J. F. Fauvarque, F. Pflüger, M. Troupel, *J. Organomet. Chem.* **1981**, *208*, 419−427.
[20] C. Amatore, A. Jutand, *Coord. Chem. Rev.* **1998**, *178−180*, 511−528.
[21] W. A. Herrmann, W. R. Thiel, C. Bromer, K. Ölefe, T. Priermeier, W. Scherer, *J. Organomet. Chem.* **1993**, *46*, 51−60.
[22] C. Amatore, G. Broeker, A. Jutand, F. Khalil, *J. Am. Chem. Soc.* **1997**, *119*, 5176−5185.

[23] J. Vicente, I. Saura-Llamas, M. G. Palin, P. G. Jones, M. C. Ramirez de Arellano, *Organometallics* **1997**, *16*, 826−833.

[24] For some examples of *ortho*-palladated complexes where two Pd^{II} moieties are bonded through a diphosphane ligand possessing a large bite angle, see: J. M. Vila, M. Gayoso, A. Fernandez, N. A. Bailey, H. Adams, *J. Organomet. Chem.* **1993**, *448*, 233−239.

[25] C. Amatore, A. Jutand, F. Khalil, M. A. M′Barki, L. Mottier, *Organometallics* **1993**, *12*, 3168−3178.

[26] Even in such cases, we have reported that the oxidative addition proceeds from a Pd^0 only ligated by the P atom after cleavage of the Pd^0-N bond, see: C. Amatore, A. Fuxa, A. Jutand, *Chem. Eur. J.* **2000**, *6*, 1474−1482.

[27] E. Riguet, M. Alami, G. Cahiez, *J. Organomet. Chem.* **2001**, *624*, 376−379.

[28] D. T. Rosevear, F. G. H. Stone, *J. Chem. Soc. A* **1968**, 164−167.

[29] M. F. Rettig, P. M. Maitlis, *Inorg. Synth.* **1977**, *17*, 134−137.

[30] M. Murakami, M. Hayashi, Y. Ito, *J. Org. Chem.* **1992**, *57*, 793−794.

[31] L. Williams, S. E. Booth, K. Undheim, *Tetrahedron* **1994**, *50*, 13697−13708.

[32] N. B. Mehta, J. Z. Strelitz, *J. Org. Chem.* **1962**, *27*, 4412−4415.

[33] L. J. Andrews, L. J. Spears, R. M. Keefer, *J. Am. Chem. Soc.* **1964**, *86*, 687−690.

[34] J. Epsztajn, A. Jozwiak, A. Szczesniak, *J. Chem. Soc., Perkin Trans. 1* **1998**, *50*, 2563−2565.

[35] W. A. Herrmann, C. Bromer, T. Priermeier, K. Ölefe, *J. Organomet. Chem.* **1994**, *481*, 97−108

[36] M. Ludwig, S. Strömberg, M. Swensson, B. Akermark, *Organometallics* **1999**, *18*, 970−991.

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