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Evidence for the Ligation of Palladium(0) Complexes by Acetate Ions: Consequences on the Mechanism of Their Oxidative Addition with Phenyl Iodide and $PhPd(OAc)(PPh_3)_2$ as Intermediate in the Heck Reaction

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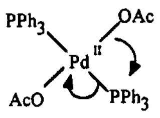
Addition of acetate anions to solutions of $Pd^0(PPh_3)_4$ results in the formation of anionic species in which the acetate ion coordinates the palladium(0) center, $Pd^0(PPh_3)_3(OAc)^-$, which is in equilibrium with the less ligated complex, $Pd^0(PPh_3)_2(OAc)^-$. The latter undergoes oxidative addition with phenyl iodide to afford a mixture of $PhPdI(PPh_3)_2$ and $PhPd(OAc)(PPh_3)_2$. Acetate ions react with $PhPdI(PPh_3)_2$ to afford $PhPd(OAc)(PPh_3)_2$. Mixtures of $Pd(OAc)_2$ and nPPh$_3$ ($n \geq 4$), commonly used as catalysts in Heck reactions, afford a palladium(0) complex that is ligated by one acetate ion, yielding the anionic species $Pd^0(PPh_3)_3(OAc)^-$ and $Pd^0(PPh_3)_2(OAc)^-$. The latter reacts with phenyl iodide. However, this reaction does not afford the expected $PhPdI(PPh_3)_2$ complex but instead affords $PhPd(OAc)(PPh_3)_2$. Reaction of $PhPd(OAc)(PPh_3)_2$ with styrene results in the formation of stilbene, demonstrating that $PhPd(OAc)(PPh_3)_2$ is an intermediate in the Heck reaction.

Introduction

We have reported in previous papers[1] that catalytic systems commonly used in Heck[2] reactions, *i.e.*, $Pd(OAc)_2(PPh_3)_2$ or a mixture of $Pd(OAc)_2$ and nPPh$_3$ ($n \geq 2$), spontaneously and quantitatively generate *in situ* a zero-valent palladium complex that can activate aryl iodides by oxidative addition. Indeed, we demonstrated that triphenylphosphine was able to reduce the bivalent palladium to a zero-valent palladium from the complex $Pd(OAc)_2(PPh_3)_2$ by an intramolecular reaction whereas triphenylphosphine was oxidized to triphenylphosphine oxide[3] according to the following mechanism (eqs 1−3): 1b

$$Pd(OAc)_2 + 2\,PPh_3 \xrightarrow{\text{fast}} Pd(OAc)_2(PPh_3)_2 \qquad (1)$$



$$\xrightarrow{\text{slow}} \text{"}Pd^0(PPh_3)(OAc)^-\text{"} + AcO\text{-}PPh_3^+ \qquad (2)$$

$$AcO\text{-}PPh_3^+ + H_2O \longrightarrow AcOH + O{=}PPh_3 + H^+ \qquad (3)$$

In the presence of excess phosphine, a stable palladium(0) was formed, but up to now it was not possible to determine precisely the fate of the acetate anion originating from reaction 2 or to determine whether or not the resulting stable palladium(0) complex was ligated by an acetate ion (eqs 4 and 5):

$$\text{"}Pd^0(PPh_3)(OAc)^-\text{"} + 2PPh_3 \xrightarrow{\text{fast}} Pd^0(PPh_3)_3 + OAc^- \qquad (4)$$

$$\text{or } Pd^0(PPh_3)_3(OAc)^- \text{ ?} \qquad (5)$$

Chloride (or bromide) anions were able to coordinate low−ligated zero-valent palladium complexes to afford anionic species[4] $[Pd^0(PPh_3)_2X_x]_n^{nx-}$ as well as more saturated complexes such as $Pd^0(PPh_3)_3Cl^-$ when chloride ions were added to $Pd^0(PPh_3)_4$.[4c] Therefore, it was of interest to investigate whether or not acetate anions were able to coordinate palladium(0) complexes, particularly in the case of palladium(0) complexes generated *in situ* from $Pd(OAc)_2$ and triphenylphosphine (reaction 4 or 5). It was also important to investigate the consequences of hypothetical ligation of palladium(0) complexes by acetate ions on the reactivity of the resulting palladium(0) complexes in oxidative additions. We report therefore our investigations concerning the fate and role of the acetate anions that are released during the intramolecular reduction of $Pd(OAc)_2(PPh_3)_2$ by triphenylphosphine. Moreover, palladium(0) complexes such as $Pd^0(PPh_3)_4$ are also efficient catalysts in

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(3) (a) Palladium(0) and BINAP oxide are formed from a mixture of $Pd(OAc)_2$ and 2BINAP. See: Ozawa, F.; Kubo, A.; Hayashi, T. *Chem. Lett.* **1992**, 2177. (b) Palladium(0) and tributylphosphine oxide are formed from a mixture of $Pd(OAc)_2$ and $1PBu_3$. See: Mandai, T.; Matsumoto, T.; Tsuji, J. *Tetrahedron Lett.* **1993**, 2513.

(4) (a) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1338. (b) When X = Cl, n = 2 and x = 2; n = 1 and x = 1 or 2. When X = Br. n = 1 and x = 1 or 2. See: (c) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375.

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Table 1. Oxidation Peak Potentials of Palladium(0) Complexes in the Absence and in the Presence of Acetate Ions

entry no.	palladium(0) complexes	E^p_{Ox} (V *vs* SCE) in DMF	E^p_{Ox} (V *vs* SCE) in THF
1	Pd^0 generated from $Pd(OAc)_2 + 5PPh_3$	+0.02	+0.13, +0.25
2	$Pd^0(PPh_3)_4$	+0.06	+0.26, +0.36
3	$Pd^0(PPh_3)_4 + 1AcO^-$ [a]	+0.02	+0.11, +0.21
4	$Pd^0(PPh_3)_4 + 2AcO^-$ [a]	+0.01	+0.14
5	$Pd^0(PPh_3)_4 + 5AcO^-$ [a]	+0.00	+0.11
6	$Pd^0(PPh_3)_4 + 10AcO^-$ [a]	−0.11	nd[b]
7	Pd^0 generated from $Pd(OAc)_2 + 10PPh_3$	+0.02	+0.13, +0.24
8	$Pd^0(PPh_3)_4 + 5PPh_3$	+0.06	+0.26, +0.41
9	$Pd^0(PPh_3)_4 + 5PPh_3 + 1AcO^-$ [a]	+0.02	+0.13, +0.23
10	$Pd^0(PPh_3)_4 + 5PPh_3 + 2AcO^-$ [a]	+0.01	+0.15
11	$Pd^0(PPh_3)_4 + 5PPh_3 + 5AcO^-$ [a]	+0.00	+0.12
12	$Pd^0(PPh_3)_4 + 5PPh_3 + 10AcO^-$ [a]	−0.01	+0.12

[a] The acetate ions were introduced as nBu_4NOAc. [b] Not determined.

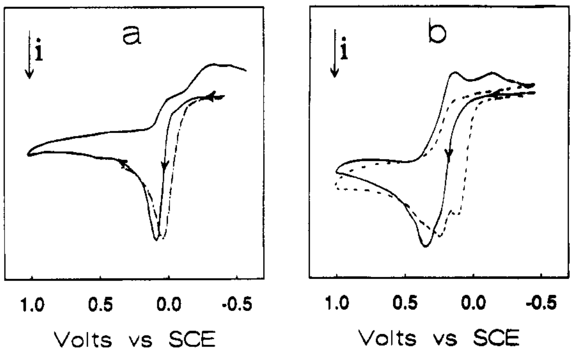

Figure 1. (a) Cyclic voltammetry of $Pd^0(PPh_3)_4$ (2 mM) in DMF (nBu_4NBF_4, 0.3 M) at a stationary gold disk electrode (ø 0.5 mm) with a scan rate of 0.2 V s^{-1}(—). Same experiment in the presence of nBu_4NOAc (1 equiv) (·–·–·). (b) Cyclic voltammetry of $Pd^0(PPh_3)_4$ (2 mM) in THF (nBu_4NBF_4, 0.3 M) (—). Same experiment in the presence of nBu_4NOAc (1 equiv) (- - -).

nucleophilic substitutions on allylic acetates in which acetate ions are continuously released during the reaction.[5] Thus the possible ligation of $Pd^0(PPh_3)_4$ by acetate ions was also investigated.

Results and Discussion

A. Ligation of Palladium(0) Complexes by Acetate Ions. Investigation by Cyclic Voltammetry. As we have already reported,[1] mixtures of $Pd(OAc)_2$ and $5PPh_3$ immediately afforded bivalent palladium complex $Pd(OAc)_2(PPh_3)_2$. This complex led spontaneously to a palladium(0) complex, which was detected by its oxidation peak in cyclic voltammetry at $E^p_{Ox} = +0.02$ V *vs* SCE, in DMF. In THF, the oxidation peak of the palladium(0) complex at $E^p_{Ox} = +0.25$ V exhibited a shoulder at +0.13 V (Table 1 and Figure 1). Formally the palladium(0) complex generated *in situ* from the mixture of $Pd(OAc)_2$ and $5PPh_3$ should be similar to $Pd^0(PPh_3)_4$ since only one PPh_3 among the five is oxidized to $O{=}PPh_3$. As already reported, tetrakis(triphenylphosphine)palladium(0), $Pd^0(PPh_3)_4$, exhibits an oxidation peak at $E^p_{Ox} = +0.06$ V in DMF. This oxidation peak is assigned to the oxidation of the main species in solution, $(DMF)Pd^0(PPh_3)_3$.[6] In THF, the oxidation peak at +0.36 V exhibits a shoulder at +0.26 V. These two oxidation peaks are respectively assigned to the oxidation of $(THF)Pd^0(PPh_3)_3$ and $Pd^0(PPh_3)_3$.[6] Comparison of the oxidation potentials of the palladium(0) complex generated *in situ* from $Pd(OAc)_2$ and $5PPh_3$ with those of $Pd^0(PPh_3)_4$ either in THF or in DMF suggests that the complex is not $Pd^0(PPh_3)_4$ (compare entries 1 and 2 in Table 1).

Addition of increasing amounts of acetate ions, introduced as nBu_4NOAc, to $Pd^0(PPh_3)_4$ in DMF results in a shift of the initial oxidation peak to less and less positive potentials (Figure 1a and Table 1). We observed that the shift was the most important in the case of the addition of the first equivalent of AcO^-. The same phenomenon was observed when increasing amounts of acetate ions were added to a solution of $Pd^0(PPh_3)_4$ containing 5 equiv of PPh_3 (Table 1). The new oxidation peak observed in the presence of acetate ions suggests that one acetate ion is able to coordinate the palladium(0) center almost quantitatively to afford an anionic species such as $Pd^0(PPh_3)_3(OAc)^-$ that is more easily oxidized than the initial complex. In THF, after introduction of 1 equiv of acetate ion to a solution of $Pd^0(PPh_3)_4$, a new oxidation peak appeared at a less positive potential, +0.21 V, with a shoulder still present at +0.11 V (Figure 1b and Table 1). In the presence of ≥2 equiv of acetate ions, only one oxidation peak was observed (Table 1). The same phenomenon was observed when increasing amounts of acetate ions were added to a solution of $Pd^0(PPh_3)_4$ containing 5 equiv of PPh_3. The most important shift was always observed in the case of the addition of the first equivalent of AcO^-. Thus it seems that in the presence of 1 equiv of AcO^- two species were formed, $(THF)Pd^0(PPh_3)_3$ and $Pd^0(PPh_3)_3(OAc)^-$, whereas only the $Pd^0(PPh_3)_3(OAc)^-$ complex was produced when >2 equiv of AcO^- was added.

These results suggest that in THF as well as in DMF acetate ions can coordinate $Pd^0(PPh_3)_3$ to afford anionic species that are more easily oxidizable than the initial complex. Comparison of the oxidation potentials of the palladium(0) complex generated *in situ* from $Pd(OAc)_2$ and $nPPh_3$ ($n \geq 5$) with those of $Pd^0(PPh_3)_4$ in the presence of one acetate ion, shows a great similitude both in THF and DMF (compare entries 1, 3, 7, and 9 in Table 1). Thus we can tentatively conclude that the palladium(0) complex generated *in situ* from mixtures of $Pd(OAc)_2$ and $nPPh_3$ is also ligated by one acetate ion, $Pd^0(PPh_3)_3(OAc)^-$ (eq 5).

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[5] (a) Trost; B. M. *Acc. Chem. Res.* 1980, *13*, 358. (b) Tsuji, J. *Tetrahedron* **1986**, *42*, 4365.

[6] Amatore, C.; Jutand, A.; Khalil, F.; Mottier, L. *Organometallics* **1993**, *12*, 3168.

Table 2. ^{31}P NMR Shifts (in ppm) of $Pd^0(PPh_3)_4$ in the Absence and in the Presence of Acetate Ions in DMF[a]

concn		+ 1AcO$^-$	+ 10AcO$^-$	+ 500AcO$^-$
11.5 mM	12.42	17.69	18.72	21.36
17.0 mM	7.12	12.75	13.12	nd[b]

[a] δ values are relative to H_3PO_4 (external reference). [b] Not determined.

However, these results are deduced from observations taken from cyclic voltammetry. We cannot exclude at this stage the possibility that the shift in the oxidation peak potentials, observable when acetate ions were added to a solution of $Pd^0(PPh_3)_4$, is not due to the formation of a new anionic species, $Pd^0(PPh_3)_3(OAc)^-$, but to a reaction of the acetate ion with the palladium(I) generated by oxidation of $Pd^0(PPh_3)_3$. Indeed, under some specific circumstances[7b] such a chemical reaction could make the $Pd^0(PPh_3)_3$ complex more easily oxidized. Also, the anionic species could exist only within an uphill equilibrium, continuously displaced by the electrode reaction.[7c]

In order to validate our above hypothesis, the effect of acetate ions on solutions of $Pd^0(PPh_3)_4$ was investigated by a technique that allows the observation of the species in solution in their initial state without any chemical or electrochemical transformation, such as ^{31}P NMR spectroscopy.

B. Ligation of Palladium(0) Complexes by Acetate Anions. Investigation by ^{31}P NMR Spectroscopy. The ^{31}P NMR spectrum of a solution of $Pd^0(PPh_3)_4$ in DMF exhibited a broad unique signal characteristic of the species $Pd^0(PPh_3)_3$, $Pd^0(PPh_3)_2$, and PPh_3 involved in a fast equilibrium (the solvent is omitted for simplification).[6,8] As evidenced in Table 2, the chemical shift of the ^{31}P NMR signal strongly depends on the overall concentration of the palladium(0) complex that affects the two equilibria 6 and 7.

$$Pd^0(PPh_3)_4 \rightleftharpoons Pd^0(PPh_3)_3 + PPh_3 \qquad (6)$$

$$Pd^0(PPh_3)_3 \rightleftharpoons Pd^0(PPh_3)_2 + PPh_3 \qquad (7)$$

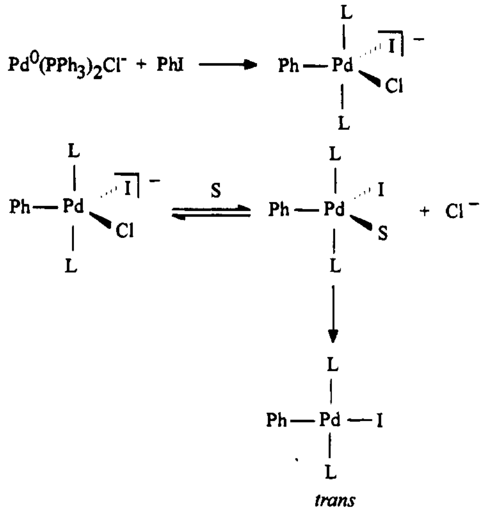
When only 1 equiv of AcO$^-$ was added as solid nBu_4NOAc to solutions of $Pd^0(PPh_3)_4$, a new broad signal was observed that was located at lower field, at around 5 ppm from the initial complex (Table 2). Whatever the palladium(0) concentration, addition of >1 equivalent of acetate also resulted in a shift of the signal to lower field, but the shift per equivalent was smaller. These results demonstrate that the acetate ions interfere in equilibria 6 and 7 by coordinating the palladium(0) complexes. The high variation of the chemical shift observed when only 1 equiv of AcO$^-$ was introduced suggests that a new species was formed, such as $Pd^0(PPh_3)_3(OAc)^-$, in the exergonic reaction 8. Since the resulting ^{31}P NMR signal was still broad, it is presumable that this reaction is followed by a fast equilibrium involving the less ligated $Pd^0(PPh_3)_2(OAc)^-$ complex and PPh_3 (reaction 9). Therefore we can assume that

$$Pd^0(PPh_3)_4 + OAc^- \rightleftharpoons Pd^0(PPh_3)_3(OAc)^- + PPh_3 \qquad (8)$$

$$Pd^0(PPh_3)_3(OAc)^- \rightleftharpoons Pd^0(PPh_3)_2(OAc)^- + PPh_3 \qquad (9)$$

acetate ions can coordinate unsaturated palladium(0) complexes to form anionic species characterized by ^{31}P NMR spectroscopy and cyclic voltammetry. Let us now examine the consequences on the oxidative addition of aryl halides to these new anionic palladium(0) complexes.

C. Characterization of the Arylpalladium Complexes Formed by Oxidative Addition of Iodobenzene with Palladium(0) Complexes Ligated by Acetate Anions. The final product resulting from the oxidative addition of triphenylphosphine ligated palladium(0) complexes with aryl halides is a stable *trans*-σ-arylpalladium complex, $ArPdXL_2$.[9] However, some of us have recently reported that when the oxidative addition was performed with a low-valent palladium(0) complex ligated by chloride, such as $Pd^0(PPh_3)_2Cl^-$, the resulting *trans-s*-arylpalladium complex was slowly formed *via* an anionic pentacoordinated σ-arylpalladium species according to the following mechanism (reactions 10−12)[10]



(10)

(11)

(12)

whereas oxidative addition of $Pd^0(PPh_3)_4$ with aryl halides rapidly affords a *trans*-σ-arylpalladium complex from the low-ligated $Pd^0(PPh_3)_2$ complex (eq 13) after deligation of two phosphine ligands through the equilibria 6 and 7.[8]

$$Pd^0(PPh_3)_2 + PhI \rightarrow \underset{trans}{PhPdI(PPh_3)_2} \qquad (13)$$

In the latter case, no intermediate has been detected, even in the presence of chloride ions. Also, triphen-

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[7] (a) The peak potential of a chemically irreversible voltammogram depends on thermodynamics (*i.e.*, structural effects) as well as on kinetics of electron transfer and homogeneous proceeding of follow-up chemical steps. In the present case, two homogeneous chemical reactions involving acetate ions and $Pd^0(PPh_3)_3$ could be tentatively considered. (b) Follow-up complexation of the Pd^I species formed upon the first electron transfer, by acetate ions, according to a classical "EC" electrochemical sequence.[7d,e] (c) An uphill pre-equilibrium involving a coordination of the Pd^0 center by acetate ions prior to the first electron transfer, according to a classical "CE" electrochemical process. See for example refs 6 and 7d: (d) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980. (e) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

[8] (a) Fauvarque, J. F.; Pflüger, F.; Troupel, M. *J. Organomet. Chem.* **1981**, *208*, 419. (b) Amatore, C.; Pflüger, F. *Organometallics* **1990**, *9*, 2276.

[9] (a) Fitton, P.; Johnson, M. P.; Mc Keon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6. (b) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

[10] (a) Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc.* **1993**, *115*, 9531. (b) Other trigonal bipyramidal structures are obviously possible see reference 32c in ref 10a.

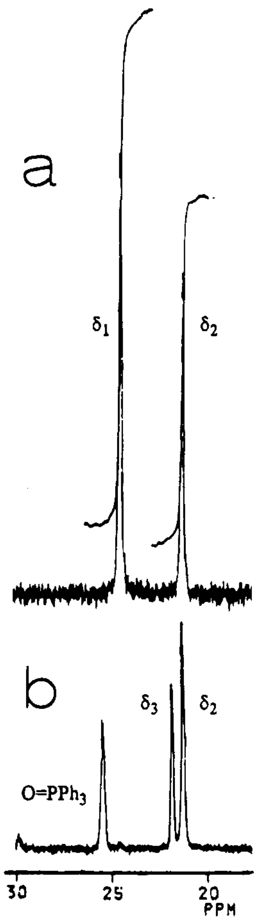

Figure 2. (a) ^{31}P NMR spectrum (162 MHz) of a mixture of *trans*-PhPdI(PPh$_3$)$_2$ (20.4 mg) and 1.5 equiv of nBu$_4$NOAc (11 mg) in 3 mL of DMF and 0.2 mL of acetone-d_6, with H$_3$PO$_4$ as an external reference. (b) ^{31}P NMR spectrum (162 MHz) of the solution resulting from the oxidative addition of PhI (1 equiv, 7 μL) to the palladium(0) complex generated *in situ* from the mixture Pd(OAc)$_2$ (14.8 mg) and 4PPh$_3$ (69 mg) in 3 mL of DMF and 0.2 mL of acetone-d_6, with H$_3$PO4 as an external reference. The ^{31}P NMR signal at 25.43 ppm is that of the triphenylphosphine oxide that was generated together with the palladium(0) complex.

ylphosphine was found to be an efficient catalyst for the formation of the *trans* complex resulting from the overall reaction 10 + 11 + 12.[10a]

When the oxidative addition with iodobenzene was performed from Pd^0(PPh$_3$)$_4$ in the presence of acetate ions (1 or 10 equiv), we found that the resulting ^{31}P NMR spectrum exhibited, in addition to the characteristic signals of *trans*-PhPdI(PPh$_3$)$_2$ at δ_1 24.44 ppm in DMF (23.42 ppm in THF) and of the free phosphine at δ_0 −5.50 ppm in DMF (−5.22 ppm in THF), an additional signal at δ_2 21.25 ppm in DMF (21.15 ppm in THF). This shows that the oxidative addition, when performed in the presence of acetate ions, affords another complex besides the usual *trans* PhPdI(PPh$_3$)$_2$ complex.[11] In order to identify the complex characterized by the signal at δ_2, we investigated whether acetate ions could react with the *trans* PhPdI(PPh$_3$)$_2$ complex or not. ^{31}P NMR spectra of solutions of the *trans* PhPdI(PPh$_3$)$_2$ complex in THF or in DMF, containing acetate ions exhibited, in addition to the signal δ_1 of the *trans* complex, a signal at δ_2 (Figure 2a) identical to that resulting from the oxidative addition described above. The ratio of the two signals was constant as a function of time, but the signal at δ_2 increased at the expense of that of δ_1 when the amount of AcO$^-$ was increased. Introduction of iodide ions resulted in the reverse effect, *viz.* increase of the signal at δ_1 at the expense of that at δ_2. An authentic sample of the *trans*-PhPd(OAc)(PPh$_3$)$_2$ complex has been synthesized (by reacting *trans*-PhPdI(PPh$_3$)$_2$ with AgOAc) and characterized by its ^{31}P NMR signal at δ_2.[12] This evidences that acetate ions react with the *trans* PhPdI(PPh$_3$)$_2$ complex to form a new complex, *trans*-PhPd(OAc)(PPh$_3$)$_2$,[13] and that this reaction is an equilibrium (eq 14). This reaction is

$$\underset{trans\ \delta_1}{\mathrm{PhPdI(PPh_3)_2}} + \mathrm{AcO^-} \overset{K}{\rightleftarrows} \underset{trans\ \delta_2}{\mathrm{PhPd(OAc)(PPh_3)_2}} + \mathrm{I^-} \qquad (14)$$

general whatever the halide of the arylpalladium halide complex, and addition of chloride ions to a solution of the *trans* PhPd(OAc)(PPh$_3$)$_2$ complex resulted in the formation of some *trans*-PhPdCl(PPh$_3$)$_2$, which was detected by its ^{31}P NMR signal at 24.40 ppm in DMF. The equilibrium constants K (eq 14) have been estimated by integration of the ^{31}P NMR signals at δ_1 and δ_2. From the values of K, collected in Table 3, we can conclude that the iodide ion is more easily substituted by the acetate ion than the chloride ion and that the substitution is easier in THF than in DMF.

Table 3. Equilibrium Constants K Determined at 27 °C for the Reaction PhPdX(PPh$_3$)$_2$ + AcO$^-$ $\rightleftarrows$ PhPd(OAc)(PPh$_3$)$_2$ + X$^-$[a,b]

X	K DMF	K THF
I	0.30 (0.45)	1.30
Br	0.10 (0.20)	0.20 (0.20)
Cl	0.04	nd[c]

[a] K = [PhPd(OAc)L$_2$][X$^-$]/[PhPdXL$_2$][AcO$^-$]. [b] Values in parentheses were determined in the presence of nBu$_4$NBF$_4$ (0.3 M). [c] Not determined.

Performing cyclic voltammetry on solutions of *trans*-PhPdX(PPh$_3$)$_2$ (X = I, Br) in DMF[14a] showed that these complexes were in equilibrium with the cationic complex PhPd(PPh$_3$)$_2^+$ (which has been synthesized by reacting *trans*-PhPdI(PPh$_3$)$_2$ with AgBF$_4$) and the corresponding equilibrium constant K_{Br} (in eq 15) has been determined by chronoamperometry.[15] Thus, the substitution of the halide by the acetate ion probably goes through a cationic complex (S$_N$1 mechanism), the latter being better solvated by DMF rather than by THF (eqs 15 and 16).[16]

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[11] Another signal was also detected at long times at δ 25.4 ppm in DMF (23.7 ppm in THF) corresponding to triphenylphosphine oxide.

[12] Some triphenylphosphine oxide was detected in the ^{31}P NMR spectrum of solutions containing PhPd(OAc)(PPh$_3$)$_2$. It seems that in solution PhPd(OAc)(PPh$_3$)$_2$ can spontaneously and slowly produce triphenylphosphine oxide *via* an intramolecular reduction in a way similar to that we have reported from Pd(OAc)$_2$(PPh$_3$)$_2$ (reactions 2 and 3).[1] The formation of triphenylphosphine oxide in high yield has also been observed in the electrochemical reduction of allylic acetates catalyzed by the complex Pd(OAc)$_2$ combined with 6PPh$_3$ probably *via* an allyl−Pd(OAc)(PPh$_3$)$_2$ complex. Torii, S.; Tanaka, H., et al. Private communication, Paris, March 1995.

[13] (a) While this paper was being written, we were informed (N. Miyaura, personal communication to A. Jutand during the 209th American Chemical Society National Meeting in Anaheim, CA, April 2−6, 1995) that (i) PhPd(OAc)(PPh$_3$)$_2$ has been synthesized simultaneously by N. Miyaura and co-workers and that (ii) Miyaura and co-workers have also observed the formation of PhPd(OAc)(PPh$_3$)$_2$ from PhPdI(PPh$_3$)$_2$ in the presence of acetate ions. (b) Preliminary results (in ii above) have already been reported by our group in ref 1a and at the same conference by A. Jutand.

$$\mathrm{PhPdX(PPh_3)_2} \overset{K_X}{\rightleftharpoons} \mathrm{PhPd(PPh_3)_2^+ + X^-} \qquad (15)$$
$$\text{with } K_{Br} = [\mathrm{PhPdBrL_2}]/[\mathrm{PhPdL_2^+}][\mathrm{Br^-}] = 3.5 \times 10^3\ \mathrm{M^{-1}}$$

$$\mathrm{PhPd(PPh_3)_2^+ + AcO^-} \overset{K_{OAc}}{\rightleftharpoons} \mathrm{PhPd(OAc)(PPh_3)_2} \qquad (16)$$
$$\text{with } K_{OAc} = [\mathrm{PhPd(OAc)L_2}]/[\mathrm{PhPdL_2^+}][\mathrm{AcO^-}]$$

Since $K = [\mathrm{PhPd(OAc)L_2}][\mathrm{Br^-}]/[\mathrm{PhPdBrL_2}][\mathrm{AcO^-}] = K_{OAc}/K_{Br}$, the equilibrium constant K_{OAc} of eq 16 can be calculated in DMF, $K_{OAc} = 7 \times 10^2\ \mathrm{M^{-1}}$. From the values of K_{OAc} and K (Table 3) we can determine $K_I = 1.5 \times 10^3\ \mathrm{M^{-1}}$ and $K_{Cl} = 1.7 \times 10^4\ \mathrm{M^{-1}}$. Comparison of the respective values of K_X (X = Cl, Br, and I) and K_{OAc} indicates that, as expected, the affinity of palladium(II) for the anion X′ in $\mathrm{PhPdX'(PPh_3)_2}$ complexes follows the order $\mathrm{Cl^- > Br^- > I^- > AcO^-}$.

Therefore, the oxidative addition of $\mathrm{Pd^0(PPh_3)_4}$ with iodobenzene performed in the presence of acetate ions affords a mixture of two complexes (eq 17).

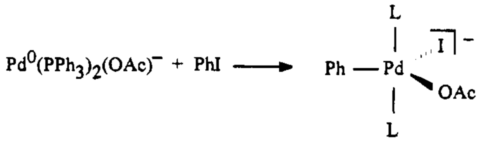
$$\mathrm{Pd^0(PPh_3)_4 + AcO^- + PhI} \rightarrow\rightarrow x\mathrm{PhPdI(PPh_3)_2} + (1-x)\mathrm{PhPd(OAc)(PPh_3)_2} + (1-x)\mathrm{I^-} + x\mathrm{AcO^-} + 2\mathrm{PPh_3} \qquad 0 < x < 1 \quad (17)$$

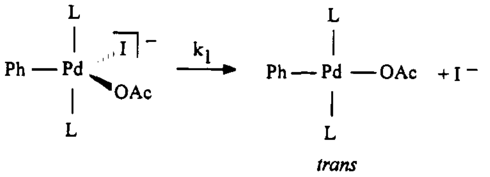
But at this stage of the study we could not determine whether the *trans* $\mathrm{PhPd(OAc)(PPh_3)_2}$ complex was formed directly from the reaction of $\mathrm{Pd(PPh_3)_2(OAc)^-}$ with iodobenzene or resulted from the equilibrium 14.

When the oxidative addition with iodobenzene was performed from the palladium(0) complex that spontaneously generated from the mixtures of $\mathrm{Pd(OAc)_2}$ and $n\mathrm{PPh_3}$ (n = 4 or 10) in DMF or THF, surprisingly the signal at δ_1 24.44 ppm in DMF (23.42 ppm in THF), characteristic of *trans*-$\mathrm{PhPdI(PPh_3)_2}$, was not detected but the signal of the *trans* $\mathrm{PhPd(OAc)(PPh_3)_2}$ complex at δ_2 21.25 ppm in DMF (21.15 ppm THF) was present with an additional signal at δ_3 21.81 ppm in DMF (21.41 ppm in THF) (Figure 2b). The signal at δ_3 was found to be identical to that of the cationic complex $\mathrm{PhPd(PPh_3)_2^+BF_4^-}$. The complex $\mathrm{PhPdI(PPh_3)_2}$ was never observed even at very long times (overnight).[17] Therefore, investigation of the oxidative addition by ^{31}P NMR spectroscopy demonstrates that the complex $\mathrm{PhPd(OAc)(PPh_3)_2}$ is the final product of the oxidative addition. Investigation of the oxidative addition by cyclic voltammetry also led to the same conclusion since the cyclic voltammogram of an authentic sample of $\mathrm{PhPd(OAc)(PPh_3)_2}$[14b] (Figure 3a) was similar to that of the final complex resulting from the oxidative addition (Figure 3b).

In an earlier paper we reported how to monitor the reactivity of the palladium(0) complex generated *in situ* from mixtures of $\mathrm{Pd(OAc)_2}$ and $n\mathrm{PPh_3}$ (n = 10) with iodobenzene by recording the variation of its oxidation plateau current as a function of time after addition of PhI.[1b] We observed that, when the electrode was polarized at +0.2 V, the oxidation current of the palladium(0) gradually dropped to zero and stabilized at this value, signifying the end of the oxidative addition. However, when the electrode was polarized at a more positive potential, *i.e.*, at +0.4 V, the current first dropped to zero and then slowly increased so as to reach a plateau (Figure 4a). Cyclic voltammetry of the final solution exhibited the characterististic oxidation peak of iodide ions (see Figure 4b) at E^p_{Ox} = +0.44 V in DMF. Thus, when the electode was polarized at a potential where iodide ions are oxidized, the decreasing part of the curve represents the kinetics of the oxidative addition of iodobenzene to the palladium(0) complex whereas the rising part of the curve represents the kinetics of release of iodide ions from an intermediate complex that affords $\mathrm{PhPd(OAc)(PPh_3)_2}$ as the final product. Since we know from above that this complex is not $\mathrm{PhPdI(PPh_3)_2}$, we are forced to conclude that the kinetic intermediate contains both acetate and iodide ions. These results suggest that the oxidative addition affords $\mathrm{PhPd(OAc)(PPh_3)_2}$ *via* a pentacoordinated phenylpalladium complex containing one iodide ion and one acetate ion according to the following mechanism (eq 9 and eqs 18 and 19):

$$\mathrm{Pd^0(PPh_3)_3(OAc)^-} \rightleftharpoons \mathrm{Pd^0(PPh_3)_2(OAc)^- + PPh_3} \qquad (9)$$


$$\mathrm{Pd^0(PPh_3)_2(OAc)^- + PhI} \longrightarrow [\mathrm{PhPdL_2(I)(OAc)}]^- \qquad (18)$$


$$[\mathrm{PhPdL_2(I)(OAc)}]^- \xrightarrow{k_1} \mathrm{Ph{-}PdL_2{-}OAc + I^-} \qquad (19)$$

The formation of rather stable pentacoordinated anionic arylpalladium complexes $\mathrm{ArPdIClL_2^-}$ has already been reported by our group in the case of the oxidative addition of $\mathrm{Pd^0(PPh_3)_2Cl^-}$ with PhI (see eq 10).[10] The value of the rate constant k_1 of the formation of $\mathrm{PhPd(OAc)(PPh_3)_2}$ from the pentacoordinated anionic species (eq 19) can be determined from the rising part of the curve in Figure 4a by plotting the variation of $\ln[(i_{lim} - i)/i_{lim}]$ (i, oxidation current of $\mathrm{I^-}$ at +0.4 V at t; i_{lim}, limit of i at infinite time) as a function of time (Figure 4c). From the slope of the straight line, one obtains $k_1 = 2.8 \times 10^{-2}\ \mathrm{s^{-1}}$. The half-life of this anionic pentacoordinated complex (≈40 s) obtained from a palladium(0) complex generated from $\mathrm{Pd(OAc)_2}$ combined with $10\mathrm{PPh_3}$ was very similar to that obtained

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[14] (a) In DMF, the cyclic voltammograms of $\mathrm{PhPdX(PPh_3)_2}$ complexes (X = I, Br, Cl) exhibited two successive irreversible reduction peaks R_1 and R_2. The ratio of the two reduction peak currents, i_1/i_2, increased when the scan rate decreased, characteristic of two species in equilibrium.[6,7d] The first reduction peak was assigned to the reduction of the cationic complex $\mathrm{PhPd(PPh_3)_2^+}$, whereas the second peak was assigned to the neutral complex $\mathrm{PhPdX(PPh_3)_2}$. Indeed, the addition of $\mathrm{X^-}$ ions to $\mathrm{PhPdX(PPh_3)_2}$ resulted in an increase of the second reduction peak at the expense of the first one.[15] (b) In DMF, the cyclic voltammogram of $\mathrm{PhPd(OAc)(PPh_3)_2}$ (Figure 3a) exhibited two successive irreversible reduction peaks. The first one, R_1 at −1.84 V, was assigned to the reduction of $\mathrm{PhPd(PPh_3)_2^+}$, and the second one, R_2 at −2.08 V, was assigned to the reduction of $\mathrm{PhPd(OAc)(PPh_3)_2}$. Addition of $\mathrm{AcO^-}$ ions resulted in an increase of the second reduction peak at the expense of the first peak.[15]

[15] Amatore, C.; Carré, E.; Jutand, A. Unpublished results, 1994.

[16] A mechanism similar to $\mathrm{S_N2}$ can probably be excluded since we have shown in a previous work that *trans* $\mathrm{PhPdX(PPh_3)_2}$ complexes did not react with halide ions $\mathrm{X'^-}$ to form pentacoordinated species such as $\mathrm{PhPdXX'(PPh_3)_2^-}$.[10a]

[17] (a) In a previous paper[1a] δ_3 was uncorrectly assigned to $\mathrm{PhPdI(PPh_3)_2}$. (b) At long times, a fourth signal was detected at δ_4 23.30 ppm in DMF that could be assigned to $\mathrm{PhPd(OH)(PPh_3)_2}$. Indeed we got the same signal by reacting $\mathrm{PhPd(PPh_3)_2^+BF_4^-}$ with water or $\mathrm{PhPdI(PPh_3)_2}$ with $\mathrm{nBu_4NOH}$. The complex $\mathrm{PhPd(OH)(PPh_3)_2}$ was recently reported to be formed from a mixture of $\mathrm{Ph_2Pd_2(\mu OH)_2(PPh_3)_2}$ and $\mathrm{PPh_3}$, but due to the equilibrium $\mathrm{Ph_2Pd_2(\mu OH)_2(PPh_3)_2 + 2PPh_3 \leftrightarrows 2PhPd(OH)(PPh_3)_2}$, the signal of $\mathrm{PhPd(OH)(PPh_3)_2}$ was not observed. See: (c) Grushin V. V.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4305.

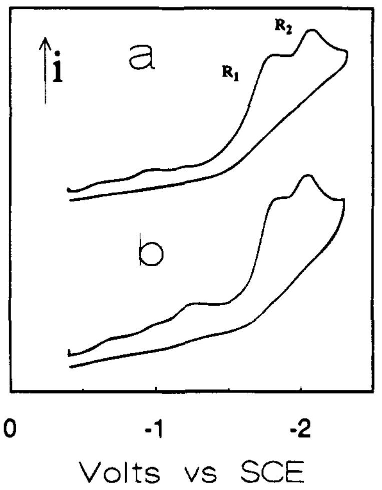

Figure 3. (a) Cyclic voltammetry of an authentic sample of PhPd(OAc)(PPh$_3$)$_2$ (2 mM) in DMF (nBu$_4$NBF$_4$, 0.3 M) at 25 °C, at a stationary gold disk electrode (ø 0.5 mm) with a scan rate of 0.2 V s^{-1}. (b) Cyclic voltammetry of the complex PhPd(OAc)(PPh$_3$)$_2$ resulting from the oxidative addition of PhI (2 mM) with the palladium(0) complex generated *in situ* from Pd(OAc)$_2$ (2 mM) and PPh$_3$ (8 mM), in DMF (nBu$_4$NBF$_4$, 0.3 M) at 25 °C.

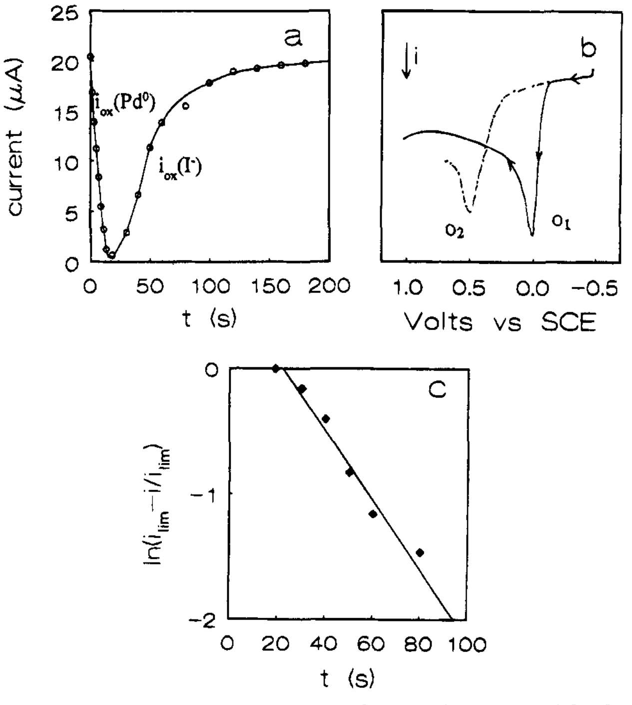

Figure 4. Oxidative addition of phenyl iodide with the palladium(0) complex generated *in situ* from Pd(OAc)$_2$ (2 mM) and PPh$_3$ (20 mM), in DMF (nBu$_4$NBF$_4$, 0.3 M) at 25 °C. (a) Variation of the oxidation plateau current at +0.4 V, at a rotating gold disk electrode (ø 2 mm; v = 0.02 Vs^{-1}; ω = 105 rad s^{-1}) in the presence of phenyl iodide (20 mM) as a function of time. (b) Cyclic voltammetry of the palladium(0) complex generated *in situ* from Pd(OAc)$_2$ (2 mM) and PPh$_3$ (20 mM), in DMF (nBu$_4$NBF$_4$, 0.3 M) at 25 °C, performed just before the oxidative addition with PhI (—). Cyclic voltammetry performed after the oxidative addition with PhI (·-·-·). (c) Variation of ln[(i_{lim} − i)/i_{lim}] as a function of time.

when Pd(OAc)$_2$ was combined with 5PPh$_3$. Therefore PPh$_3$ does not seem to catalyze the formation of the *trans* PhPd(OAc)(PPh$_3$)$_2$ complex from the anionic pentacoordinated PhPdI(OAc)(PPh$_3$)$_2$$^-$, a result that was observed for the formation of the *trans* PhPdI(PPh$_3$)$_2$ complex from PhPdICl(PPh$_3$)$_2$$^-$.[10a]

Although iodide ions were released from reaction 19, they did not react with PhPd(OAc)(PPh$_3$)$_2$ to produce PhPdI(PPh$_3$)$_2$ according to the equilibrium 14, since PhPdI(PPh$_3$)$_2$ was never observed in the ^{31}P NMR spectrum recorded after the oxidative addition. This suggests that the iodide ions, liberated in reaction 19, were not completely free. The formation of the palladium(0) complex from the mixtures of Pd(OAc)$_2$ and nPPh$_3$ is concomitant with the formation of AcOH and H$^+$ according to reaction 3. Iodide ions might be involved in an equilibrium with the proton ($I^- + H^+ \rightleftharpoons HI$) and therefore might not be able to react significantly with PhPd(OAc)(PPh$_3$)$_2$. This hypothesis was confirmed by the fact that when no protons were present in the medium, *i.e.*, when the oxidative addition with PhI was performed from a mixture of Pd^0(PPh$_3$)$_4$ and AcO$^-$, both PhPdI(PPh$_3$)$_2$ and PhPd(OAc)(PPh$_3$)$_2$ were produced.

We can thus assume that the oxidative addition of iodobenzene with the palladium(0) complex formed *in situ* from the mixtures of Pd(OAc)$_2$ and nPPh$_3$, does not afford the *trans* PhPdI(PPh$_3$)$_2$ complex but rather the *trans* PhPd(OAc)(PPh$_3$)$_2$ complex. This occurs most presumably *via* pentacoordinated species PhPdI(OAc)(PPh$_3$)$_2$$^-$. Conversely, a mixture of *trans*-PhPdI(PPh$_3$)$_2$ and *trans*-PhPd(OAc)(PPh$_3$)$_2$ is obtained when the oxidative addition is performed from a mixture of Pd^0(PPh$_3$)$_4$ and AcO$^-$.

D. Reactivity of Palladium(0) Complexes Ligated by Acetate Anions in Oxidative Addition with Iodobenzene in DMF at 25 °C. We established above that the products resulting from the oxidative addition strongly depend on the precursor of the palladium(0) complex. We wish now to investigate the reactivity of different palladium(0) complexes in the oxidative addition as a function of the precursor. As mentioned above and in our previous paper,[1b] it is possible to monitor the reactivity of palladium(0) complexes in oxidative addition with phenyl iodide by recording its oxidation plateau current at +0.2 V as a function of time (Figure 5a). A plot of the ratio i_0/i as a function of time, resulted in a straight line ($i_0/i = k_{app}C_0t + 1$, when [PhI] = [Pd^0] = C_0), demonstrating that the oxidative addition was first order in palladium(0) and in iodobenzene (Figure 5b). The value of the apparent rate constant k_{app} of the oxidative addition could then be deduced from the slope of the straight line (eq 20).

$$\text{“Pd}^0\text{L}_n\text{, AcO}^-\text{”} + \text{PhI} \xrightarrow{k_{app}} \text{PhPdXL}_2 + (n-2)\text{L} \quad (20)$$

From the values of k_{app} determined when the oxidative addition of PhI with Pd^0(PPh$_3$)$_4$ was performed in the absence or in the presence of acetate (Table 4, entries 1−4) we can deduce that the presence of acetate anions does not have a significant influence on the apparent rate constant of the oxidative addition. In the absence of acetate, it is reported that the low-ligated palladium(0) complex Pd^0(PPh$_3$)$_2$ is more reactive in oxidative addition than the more ligated complex Pd^0(PPh$_3$)$_3$. Its overall rate depends on its concentration, which is controlled by the value of the equilibrium constant K (eq 7).[8]

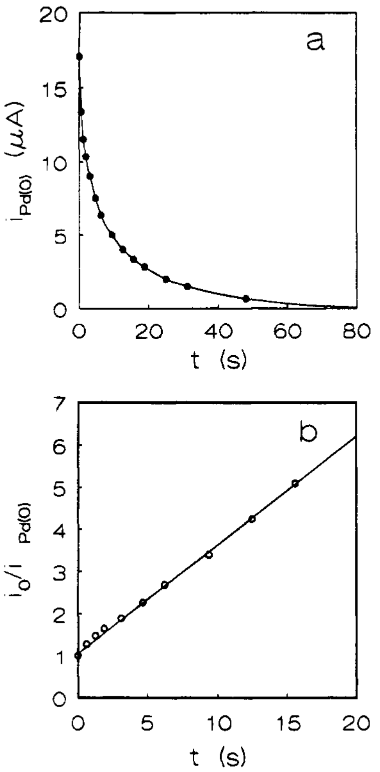

Figure 5. Oxidative addition of phenyl iodide with the palladium(0) complex quantitatively generated *in situ* from $Pd(OAc)_2$ (2 mM) and PPh_3 (6 mM), in DMF (nBu_4NBF_4, 0.3 M) at 25 °C. (a) Variation of the oxidation plateau current $i_{Pd(0)}$ at +0.2 V, at a rotating gold disk electrode (ø = 2 mm; v = 0.02 V s^{-1}; ω = 105 rad s^{-1}) in the presence of phenyl iodide (2 mM) as a function of time. (b) Variation of i_0/i as a function of time.

$$\begin{tikzcd}
Pd^0(PPh_3)_3 \arrow[r, leftrightharpoons] & Pd^0(PPh_3)_2 + PPh_3 \arrow[d, "k", "+PhI"'] & K \quad (7) \\
& PhPdI(PPh_3)_2 &
\end{tikzcd}$$

In the presence of an excess of phosphine, the corresponding apparent rate constant of the oxidative addition is given by the relation $k_{app} = kK/[PPh_3]$.[8] In the presence of acetate ions, the corresponding apparent rate constant of the oxidative addition is: $k'_{app} = k'K'/[PPh_3]$ (eq 9).

$$\begin{tikzcd}
Pd^0(PPh_3)_3(OAc)^- \arrow[r, leftrightharpoons] & Pd^0(PPh_3)_2(OAc)^- + PPh_3 \arrow[d, "k'", "+PhI"'] & K' \quad (9) \\
& PhPdI(PPh_3)_2 + PhPd(OAc)(PPh_3)_2 &
\end{tikzcd}$$

The complex $Pd^0(PPh_3)_2(OAc)^-$ would be the reactive species rather than $Pd^0(PPh_3)_2$. Indeed, since the rate of the oxidative addition was not sensitive to the acetate concentration, one can exclude the participation of the following equilibrium (eq 21)

$$Pd^0(PPh_3)_2(OAc)^- \rightleftharpoons Pd^0(PPh_3)_2 + AcO^- \quad (21)$$

which would yield an apparent rate constant $k''_{app} = k''K''/[AcO^-]$.

Surprisingly, the fact that the rate does not depend on the acetate concentration implies that the value of $k'K'$ is very close to that of kK. The ligation of $Pd^0(PPh_3)_2$ by one acetate ion produces a species $Pd^0(PPh_3)_2(OAc)^-$ that ought to be more nucleophilic and more reactive in the oxidative addition with PhI. Thus k' is expected to be higher than k, which implies that $K' < K$.

However, one observes from the values of k_{app} (Table 4, compare entries 2 and 5) that the oxidative addition with phenyl iodide was slightly faster with the palladium(0) generated from the mixture of $Pd(OAc)_2$ and $5PPh_3$ than with $Pd^0(PPh_3)_4$ and $1AcO^-$, although the two systems are formally equivalent, since one triphenylphosphine is oxidized to triphenylphosphine oxide in the first system. In some way, it could seem that internal acetate ions play a more efficient role than external ones. However, it must be noted that the generation of the palladium(0) complex from mixtures of $Pd(OAc)_2$ and $nPPh_3$ is concomitant with the formation of triphenylphosphine oxide and protons (reaction 3). These two species may interfere in the kinetics of the oxidative addition. It has been postulated that phosphine oxide may coordinate palladium complexes,[3b] but we observed that adjunction of 1 equiv of $O{=}PPh_3$ to the mixture of $Pd^0(PPh_3)_4$ and $1AcO^-$ did not change the value of the apparent rate constant of the oxidative addition with PhI. The role of the proton may be the complexation of the reactive anionic species $Pd^0(PPh_3)_2(OAc)^-$. In order to clarify the role of the proton, the oxidative addition was performed with the palladium(0) complex generated from the mixture $Pd(OAc)_2$ and $5PPh_3$ but in the presence of 3 equiv of a base, NEt_3. Under these conditions the value of the apparent rate constant of the oxidative addition was k_{app} = 22 M^{-1} s^{-1}, a value similar to that found for the oxidative addition performed from the mixture of $Pd^0(PPh_3)_4$ and $nAcO^-$ (entries 2–4, Table 4) where, of course, no proton was present. Therefore protons appear to play the same role with $Pd^0(PPh_3)_2(OAc)^-$ as cations do with the anionic species $Pd^0(PPh_3)_2Cl^-$, *i.e.*, coordinating the negatively charged palladium(0) species with the result of enhancing its reactivity.[4c]

In the presence of excess phosphine (more than 5 equiv per palladium(0)) the reactivity of the palladium(0) complex did not depend significantly on its precursor (Table 4, compare entries 7–9). As expected the oxidative addition became slower upon increasing the phosphine concentration. This is rationalized considering that the concentration of the reactive species $Pd^0(PPh_3)_2(OAc)^-$ became smaller because the presence of an excess of phosphine results in the shift of the equilibrium 9 to its left-hand side.

As expected, the most reactive palladium(0) complex was that generated from the mixture of $Pd(OAc)_2$ and $3PPh_3$ (Table 4, entry 6) in which the resulting palladium(0), $Pd^0(PPh_3)_2(OAc)^-$, could not be ligated by more than two phosphines and is thus the only Pd(0) species in solution. Therefore mixing $Pd(OAc)_2$ and $3PPh_3$ allows the direct and quantitative synthesis of $Pd^0(PPh_3)_2(OAc)^-$ ligated by only two phosphines, which undergoes a fast reaction with iodobenzene. In this case, since no extra phosphine is present in solution, we do not measure the value of an apparent rate constant but measure directly the value of the rate constant k' of the intrinsic oxidative addition (eq 22).

$$Pd^0(PPh_3)_2(OAc)^- + PhI \xrightarrow{k_2} PhPd(OAc)(PPh_3)_2 + I^-$$
$$k_2 = 140\ M^{-1}\ s^{-1} \text{ in DMF at 25 °C} \quad (22)$$

Table 4. Apparent Rate Constant k_{app} of the Oxidative Addition of Palladium(0) Complexes with PhI as a Function of Their Precursors in DMF at 25 °C

entry no.	precursor of "Pd⁰"	main species in solution	k_{app} (M^{-1} s^{-1})
1	$Pd^0(PPh_3)_4$	$Pd^0(PPh_3)_3$ + 1PPh_3	25
2	$Pd^0(PPh_3)_4$ + 1AcO^-	$Pd^0(PPh_3)_3(OAc)^-$ + 1PPh_3	21
3	$Pd^0(PPh_3)_4$ + 10AcO^-	$Pd^0(PPh_3)_3(OAc)^-$ + 1PPh_3 + 9AcO^-	24
4	$Pd^0(PPh_3)_4$ + 100AcO^-	$Pd^0(PPh_3)_3(OAc)^-$ + 1PPh_3 + 99AcO^-	26
5	$Pd(OAc)_2$ + 5PPh_3	$Pd^0(PPh_3)_3(OAc)^-$ + 1PPh_3 + O=PPh_3	41
6	$Pd(OAc)_2$ + 3PPh_3	$Pd^0(PPh_3)_2(OAc)^-$ + O=PPh_3	140
7	$Pd^0(PPh_3)_4$ + 5PPh_3	$Pd^0(PPh_3)_3$ + 6PPh_3	9.5
8	$Pd^0(PPh_3)_4$ + 5PPh_3 + 1AcO^-	$Pd^0(PPh_3)_3(OAc)^-$ + 6PPh_3	12.5
9	$Pd(OAc)_2$ + 10PPh_3	$Pd^0(PPh_3)_3(OAc)^-$ + 6PPh_3 + O=PPh_3	12

Scheme 1

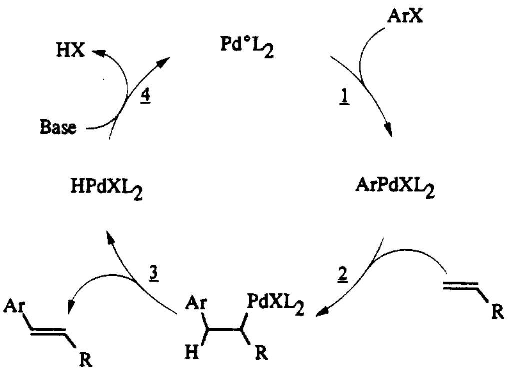

Table 5. Reaction of Styrene with Isolated PhPdI(PPh₃)₂ Complex and with PhPd(OAc)(PPh₃)₂ Resulting from the Oxidative Addition of PhI with the Palladium(0) Complex Generated *in Situ* from Pd(OAc)₂ and 4PPh₃ in DMF at 25 °C

entry no.	$PhPdX(PPh_3)_2$	NEt_3 (no. of equiv)	time (h)	stilbene (%)[a]
1	$PhPd(OAc)(PPh_3)_2$[b]	0	20	35
2	$PhPd(OAc)(PPh_3)_2$[b]	1[c]	17	70, 70
3	$PhPd(OAc)(PPh_3)_2$[b]	3[c]	19	75, 66
4	$PhPdI(PPh_3)_2$[d]	0	24	0
5	$PhPdI(PPh_3)_2$[d] + 2AcO^-	0	22	57
6	$PhPdI(PPh_3)_2$[d] + 2AcO^-	1	48	72
7	$PhPd(PPh_3)_2^+BF_4^-$ [e]	0	25	27
8	$PhPd(PPh_3)_2^+BF_4^-$ [e]	1	18	22

[a] Yields are relative to the initial $PhPdX(PPh_3)_2$ complexes. [b] Reaction performed on the $PhPd(OAc)(PPh_3)_2$ complex resulting from the oxidative addition of PhI with the palladium(0) complex generated *in situ* from $Pd(OAc)_2$ and 4PPh_3. Styrene/PhI/$Pd(OAc)_2$ = 100/1/1 with [$Pd(OAc)_2$] = 2 mM. [c] NEt_3 was introduced at the beginning of the reaction together with the mixture of $Pd(OAc)_2$ and 4PPh_3. [d] Reaction performed on an authentic sample of $PhPdI(PPh_3)_2$ in the absence or presence of nBu_4NOAc. Styrene/$PhPdI(PPh_3)_2$ = 100/1 with [$PhPdI(PPh_3)_2$] = 2 mM. [e] Reaction performed on an authentic sample of $PhPd(PPh_3)_2^+BF_4^-$ with Styrene/$PhPd(PPh_3)_2^+BF_4^-$ = 100/1 and [$PhPd(PPh_3)_2^+BF_4^-$] = 2 mM.

E. PhPd(OAc)(PPh₃)₂ as Intermediate in the Heck Reaction. Mixtures of $Pd(OAc)_2$ and $n$$PPh_3$ (n ≥ 2) are efficient catalysts for Heck reactions (eq 23).[2]

$$ArX + R{-}CH{=}CH_2 + NR'_3 \xrightarrow{Pd(OAc)_2 + nPPh_3} R{-}CH{=}CH{-}Ar + HNR'^{+}_3X^- \quad (23)$$

The mechanism generally accepted is recalled in Scheme 1.[2h] The rate determining step of the catalytic cycle has never been clearly established. There is general agreement on the fact that the first step of the reaction is oxidative addition of a palladium(0) complex with the aryl halide ArX (step 1) to form an $ArPdXL_2$ complex prone to add on the olefin (step 2). In the present study, we have observed that complexes such as $ArPdX(PPh_3)_2$ (step 1) were not formed during the oxidative addition but that the final product was $ArPd(OAc)(PPh_3)_2$ involved in an equilibrium with the cationic complex $ArPd(PPh_3)_2^+$ (eq 16). It is thus of interest to determine the real intermediate involved in the Heck reaction, *i.e.*, the arylpalladium(II) complex able to react with olefins (step 2). The reaction was followed by cyclic voltammetry with styrene as the olefin. The final expected product, *trans*-stilbene, can be easily detected by its reduction peak at −2.20 V, which is located at a more negative potential than that of $PhPd(OAc)(PPh_3)_2$ (−2.04 V) and at a less negative potential than the reduction potential of styrene (−2.60 V).

From the results collected in Table 5, we observe that under our experimental conditions (DMF, 20 °C) stilbene was formed by reacting styrene with the complex $PhPd(OAc)(PPh_3)_2$ resulting from the oxidative addition of PhI (1 equiv) with the palladium(0) complex generated from the mixture of $Pd(OAc)_2$ and 4PPh_3. Yields were higher when some triethylamine was present (entries 1−3). The amine is usually described as a reagent able to regenerate the palladium(0) catalyst in step 4 (Scheme 1), *i.e.*, in the step following the formation of the final product. Since we have operated under non catalytic conditions in which the iodobenzene was in stoichiometric proportion relative to the palladium(0) complex, it seems that the amine interferes also in previous steps, unless step 3 is an equilibrium. This latter hypothesis was disproved by the fact that introduction of NEt_3 at the end of the reaction did not improve the yield of stilbene. In a previous study we demonstrated that acetic acid and a proton were formed with the palladium(0) generated from $Pd(OAc)_2$ and $n$$PPh_3$ (eq 3).[1b] Therefore, in stoichiometric conditions the role of the amine might be the neutralization of the medium. The role of the amine might, however, become more complex under catalytic conditions by regenerating the palladium(0) complex (see step 4).

The role of $PhPd(OAc)(PPh_3)_2$ as intermediate in Heck reactions is confirmed by the results of entries 4−6 in Table 5. While $PhPdI(PPh_3)_2$ did not react with styrene under our experimental conditions,[18] the adjunction of acetate ions allowed the reaction to proceed. Since we have demonstrated above that acetate ions were able to substitute the iodide ion from $PhPdI(PPh_3)_2$ to afford $PhPd(OAc)(PPh_3)_2$ (eq 14), this establishes that PhPd-

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[18] (a) Some $ArPdX(PPh_3)_2$ complexes can react with styrene but under more drastic conditions than ours, at least at 80 °C. See: (b) Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133. c) Andersson, C. M.; Hallberg, A.; Doyle Daves, G., Jr. *J. Org. Chem.* **1987**, *52*, 3529.

$(OAc)(PPh_3)_2$ is essential and is the species that reacts with the olefin.

The cationic complex $PhPd(PPh_3)_2^+$ formed by dissociation of $PhPd(OAc)(PPh_3)_2$ (eq 16) also reacts with styrene[19] but afforded lower yields and required longer reaction times whatever the triethylamine concentration (Table 5, entries 7 and 8). Since $PhPd(OAc)(PPh_3)_2$ reacts faster than the cationic complex, it cannot react through its cationic complex *via* eq 16. The fact that triethylamine did not affect the yield of the reaction with the cationic complex when no acid was present confirms our above conclusion concerning the role of the amine as a neutralizing reagent.

Therefore we can assume that the first two steps of the catalytic cycle presented in textbooks (Scheme 1) are not operating under the conditions of the Heck reaction, at least when the catalyst is ligated by triphenylphosphine which was the only ligand investigated here.[19,21,22] Indeed, we have demonstrated that $ArPd(OAc)(PPh_3)_2$ complexes are formed by the oxidative addition and give rise to Heck reactions. Further kinetic investigations to clarify this mechanism are presently on the way.

Conclusion

Acetate anions can coordinate palladium(0) centers to form unprecedented anionic species that are in equilibrium, $Pd^0(PPh_3)_3(OAc)^-$ and $Pd^0(PPh_3)_2(OAc)^-$. Such species are formed when acetate ions are added to solutions of $Pd^0(PPh_3)_4$ or when the palladium(0) is generated *in situ* from mixtures of $Pd(OAc)_2$ and $nPPh_3$. It is noteworthy that the latter mixtures are the usual catalyst precursors in the Heck reactions. In both cases the low-ligated complex $Pd^0(PPh_3)_2(OAc)^-$ undergoes an oxidative addition with iodobenzene. In the first case a mixture of $PhPdI(PPh_3)_2$ and $PhPd(OAc)(PPh_3)_2$ is produced, whereas in the second case only $PhPd(OAc)(PPh_3)_2$ is detected. The latter complex reacts with styrene to form stilbene, and this new complex was established as an essential intermediate of the Heck reaction, at least within the first catalytic cycle.

Therefore acetate anions can coordinate palladium(0) complexes as halides have been reported to do.[4] A consequence is that low-ligated palladium(0) complexes such as $Pd^0(PPh_3)_3$ or $Pd^0(PPh_3)_2$ do not exist as soon as halide or acetate anions are present in solution. The result of the ligation of palladium(0) complexes by anions is the formation of new intermediates in the oxidative addition with phenyl iodide, such as $PhPdICl(PPh_3)_2^-$[10] or $PhPdI(OAc)(PPh_3)_2^-$, which is a precursor of new final complexes such as $PhPd(OAc)(PPh_3)_2$.

Experimental Section

^{31}P NMR spectra were recorded on a Bruker spectrometer (162 MHz) using H_3PO_4 as an external reference. ^1H NMR spectra were recorded on a Bruker spectrometer (250 MHz). All experiments were performed under argon.

Chemicals. DMF was distilled over calcium hydride, dichloromethane over CaH_2, and petroleum ether over P_2O_5. Iodobenzene was from a commercial source (Janssen) and used after filtration on alumina. Triethylamine was commercial and distilled. $Pd(OAc)_2$, AgOAc, $AgBF_4$, nBu_4NI, styrene, and triphenylphosphine were from commercial sources (Janssen or Aldrich). nBu_4NOAc was synthesized as previously reported.[1a] Authentic samples of $PhPdX(PPh_3)_2$ (X = I,[9] Br,[9] and Cl[24]) were prepared according to described procedures.

Synthesis of $PhPd(OAc)(PPh_3)_2$. The synthesis was carried out using Schlenk techniques under argon. To 0.1 g (0.12 mmol) of $PhPdI(PPh_3)_2$ in 15 mL of CH_2Cl_2 was added 0.04 g (0.24 mmol) of AgOAc. The mixture was stirred at room temperature and in the dark. A grey precipitate was formed. After filtration of the precipitate and evaporation of the filtrate, 0.035 g of a beige precipitate was collected. Yield: 38%. ^{31}P NMR (162 MHz, DMF, acetone-d_6, H_3PO_4) δ, ppm: 21.36. ^1H NMR (250 MHz, $CDCl_3$, TMS) δ, ppm: 2.01 (m, 3H), 6.31 (t, 1H, J = 7.5 Hz), 6.55 (d, 2H, J = 7.5 Hz), 6.63 (t, 2H, J = 7.5 Hz), 7.25 (m, 12H), 7.42 (m, 18H).

Synthesis of $PhPd(PPh_3)_2^+BF_4^-$. The synthesis was carried out using Schlenk techniques under argon. To 0.2 g (0.24 mmol) of $PhPdI(PPh_3)_2$ in 20 mL of CH_2Cl_2 was added 0.07 g (0.36 mmol) of $AgBF_4$. The mixture was stirred for 4 h at room temperature and in the dark. A black precipitate was formed. After filtration of the precipitate and almost complete evaporation of the filtrate, the resulting mixture was poured into a large volume of petroleum ether. A pink-orange precipitate was formed, filtered, dried under vacuum, and stored under argon. A 0.12 g amount of an orange powder was collected. Yield: 62%. ^{31}P NMR (162MHz, DMF, acetone-d_6, H_3PO_4) δ, ppm: 21.70. ^1H NMR (250 MHz, $CDCl_3$, TMS) δ, ppm: 7.38 (m, 2H), 7.49 (dd, 2H, J = 7.5 Hz), 7.53 (t, 1H, J = 7.5 Hz), 7.62 (dd, 6H, J = 7.5 Hz, J = 2 Hz), 7.68 (dd, 6H, J = 7.5 Hz, J = 2 Hz), 7.78 (t, 6H, J = 7.5 Hz), 7.79 (t, 6H, J = 7.5 Hz), 7.91 (td, 6H, J = 7.5 Hz, J = 2 Hz). Anal. Calcd for $C_{42}H_{35}P_2PdBF_4$: C, 63.46; H, 4.44. Found: C, 63.32; H, 4.40.

Electrochemical Setup and Procedure for Cyclic Voltammetry. Cyclic voltammetry was performed with a homemade potentiostat and a wave-form generator, PAR model 175. Cyclic voltammograms were recorded with a Nicolet 3091 digital oscilloscope. Experiments were carried out in a three-electrode cell connected to a Schlenk line. The cell was equipped with a double envelope in order to perform the reactions at constant temperature, 25 °C, using a Lauda M3 thermostat. The counter electrode was a platinum wire of *ca.* 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge (3 mL) filled with a 0.3 M nBu_4NBF_4 solution in DMF. A 12-mL volume of DMF containing 0.3 M nBu_4NBF_4 was poured into the cell. A 27.7 mg amount (2×10^{-3} M) of $Pd^0(PPh_3)_4$ was then added. Cyclic voltammetry was performed at a stationary disk electrode (a gold disk made from cross section of wire, 0.5 mm diameter, sealed into glass) at a scan rate of 0.2 V s^{-1}. Suitable amounts of required reagents (*e.g.*, nBu_4NOAc) were then added to the cell, and the cyclic voltammetry was performed again.

In another experiment, a 5.4 mg amount (2×10^{-3} M) of $Pd(OAc)_2$ was added followed by the suitable amount of triphenylphosphine. The formation of the Palladium(0) complex from the mixture $Pd(OAc)_2$ and $nPPh_3$ was monitored by steady state cyclic voltammetry at a rotating disk electrode (a gold disk, 2 mm i.d.) inserted into a Teflon holder (Tacussel EDI 65109) at a scan rate of 0.02 V s^{-1} and an angular velocity of 105 rad s^{-1} (Tacussel controvit). The potential was set on

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[19] Cationic arylpalladium complexes have been postulated as intermediates in the Heck reaction.[20] This hypothesis is generally developed in the case of bidentate ligands[2i,21,22] or when the Heck reaction is performed from aryl triflates[2i,22] that afford cationic complexes by reacting with palladium(0) complexes in the absence of any anions.[23]

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the plateau of the oxidation wave of the palladium(0) complex, and the oxidation current was monitored as a function of time. When the limit of the oxidation current was reached (100% conversion), the suitable amount of iodobenzene was added to the cell and the oxidation current of the palladium(0) complex was recorded as a function of time to follow the kinetics of oxidative addition with PhI.[1b] Cyclic voltammetry was performed on the resulting solution in reduction and in oxidation in order to characterize the products resulting from the oxidative addition.

Procedure for the Heck Reaction. From $PhPd(OAc)(PPh_3)_2$: A 5.4 mg amount (0.024 mmol) of $Pd(OAc)_2$ was added to the cell followed by a 25 mg amount (0.096 mmol) of triphenylphosphine. The formation of the palladium(0) complex was monitored by steady state cyclic voltammetry at a rotating disk electrode (same conditions as above). When the limit of the oxidation current was reached (100% conversion), 2.7 μL (0.024 mmol) of iodobenzene was added. Cyclic voltammetry was performed on the resulting solution and exhibited the characteristic reduction peaks of $PhPd(OAc)(PPh_3)_2$. A 275 μL amount (2.4 mmol) of styrene was added. The formation of *trans*-stilbene was followed by cyclic voltammetry (reduction peak at −2.20 V) performed as a function of time. The yield in *trans*-stilbene was determined by cyclic voltammetry by comparison of the magnitude of its reduction peak current with that of a known amount of an authentic sample of *trans*-stilbene.

The same reactions were performed in the presence of various amounts of NEt_3 introduced at the beginning of the reaction together with $Pd(OAc)_2$ and $4PPh_3$.

From $PhPdI(PPh_3)_2$: A 20 mg amount (0.024 mmol) of $PhPdI(PPh_3)_2$ was added to the cell followed by 275 μL (2.4 mmol) of styrene, and the reaction was followed by cyclic voltammetry as described above. In another experiment a 14.4 mg amount (0.048 mmol) of nBu_4NOAc was added to the solution followed (or not) by addition of 3.5 μL (0.024 mmol) of NEt_3.

From $PhPd(PPh_3)_2{}^+BF_4{}^-$: A 19 mg amount (0.024 mmol) of $PhPd(PPh_3)_2{}^+BF_4{}^-$ was added to the cell followed by 275 μL (2.4 mmol) of styrene. The reaction was followed by cyclic voltammetry as described above. In another experiment, 3.5 μL (0.024 mmol) of NEt_3 was added to the solution.

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