Role and Effects of Halide Ions on the Rates and Mechanisms of Oxidative Addition of Iodobenzene to Low-Ligated Zerovalent Palladium Complexes $Pd^0(PPh_3)_2$

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Abstract: The role and effect of chloride and bromide ions on the intimate mechanisms and rates of oxidative addition of iodobenzene to electrogenerated low-ligated zerovalent palladium complex "$Pd^0(PPh_3)_2$" are examined and discussed on the basis of ^{31}P NMR and transient electrochemistry. It is shown that $Pd^0(PPh_3)_2$ actually consists of a mixture of three anionic species, $[Pd^0(PPh_3)_2Cl]_2^{2-}$ (A), $Pd^0(PPh_3)_2Cl^-$ (B), and $Pd^0(PPh_3)_2Cl_2^{2-}$ (C), which are in rapid equilibrium within the time scale of their oxidative addition by iodobenzene. This stabilization of low-ligated zerovalent palladium by chloride ions occurs also during the oxidative addition of iodobenzenes to the ubiquitous $Pd^0(PPh_3)_4$. This shows that the results of this study may be transposed to more classical procedures of generation of the active zerovalent palladium complex $Pd^0(PPh_3)_2$, and also affords a tentative explanation of the effect of chloride ions in palladium-catalyzed nucleophilic substitutions or in the Heck reaction.

Introduction

Zerovalent palladium complexes are efficient catalysts of aromatic and vinylic nucleophilic substitution[1] or of arylation of olefins, the Heck reaction.[2] These reactions have been established to proceed via catalytic cycles triggered by oxidative addition[1-3] of the aromatic or vinylic halide to the zerovalent palladium complex to afford a σ-arylpalladium(II) or σ-vinylpalladium(II) insertion complex, e.g.

$$ArX + Pd^0L_n \rightarrow ArPd^{II}L_2X + (n-2)L \quad (1)$$
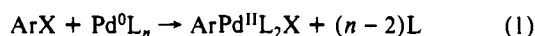
In substitution reactions, the latter is supposed to undergo then a nucleophilic attack followed by reductive elimination[1]

$$ArPd^{II}L_2X + Nu^- \rightarrow ArNu + Pd^0L_2 + X^- \quad (2)$$

which regenerates the zerovalent palladium catalyst. In the Heck reaction, reaction 1 is thought to proceed by insertion of the olefin in the aryl–palladium bond, followed by β-elimination of hydrogen to afford "X–Pd–H", from which the catalyst is regenerated by reaction with a base:[2]

$$ArPd^{II}L_2X + CHR_1=CHR_2 + B^- \rightarrow$$
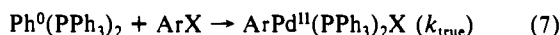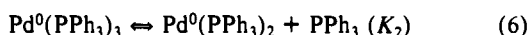$$ArCR_1=CHR_2 + BH + X^- + Pd^0L_2 \quad (3)$$
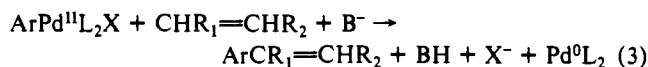
A usual catalyst of the above nucleophilic substitutions is the stable zerovalent palladium complex tetrakis(triphenylphosphine)palladium(0),[1] which has been shown by ^{31}P NMR to be present in solution as $Pd^0(PPh_3)_3$.[7] This is rationalized by considering that loss of phosphine in eq 4 is irreversible under the usual experimental conditions ($K_1 \gg$ [PPh_3]):

$$Pd^0(PPh_3)_4 \rightleftharpoons Pd^0(PPh_3)_3 + PPh_3 \quad (K_1) \quad (4)$$
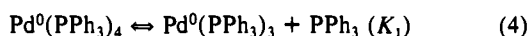
However, $Pd^0(PPh_3)_3$ is not directly involved in oxidative addition, since the latter obeys a rate law first order in palladium(0) and in aromatic halide but also reciprocal first order in phosphine:[8]

$$d[Pd^0]/dt = d[ArX]/dt = -k_{mes}[Pd^0][ArX]/[PPh_3] \quad (5)$$

Such a rate law implies that $Pd^0(PPh_3)_3$ must undergo an endergonic phosphine loss ($K_2 \ll$ [PPh_3]) before reacting with the aromatic halide:[8]

$$Pd^0(PPh_3)_3 \rightleftharpoons Pd^0(PPh_3)_2 + PPh_3 \quad (K_2) \quad (6)$$

$$Ph^0(PPh_3)_2 + ArX \rightarrow ArPd^{II}(PPh_3)_2X \quad (k_{true}) \quad (7)$$

Indeed the rate law predicted for the reaction sequence in eqs 6 and 7 is

$$d[Pd^0]/dt = d[ArX]/dt = -k_{true}K_2[Pd^0][ArX]/[PPh_3] \quad (8)$$

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Table I. Peak Potentials of $Pd^{II}X_2(PPh_3)_2$ at 0.2 V s^{-1} [a]

	E^p (V vs SCE)		
X	R or R_1	R_2	O[b]
Cl	-1.04_0	-1.25_0	0.10^0
Br	-0.83_0	-1.07_5	0.12_0
I	-0.72_0	-0.94_0	0.12_5

[a] 2 mM in THF/0.3 M n-Bu$_4$NBF$_4$, 20 °C. [b] In absence of added halide ions.

which shows that k_{mes} in eq 5 is equal to $k_{true}K_2$. A well-recognized means of increasing the apparent[9] rate of oxidative addition

(1) For reviews, see: (a) Kumada, M. *Pure Appl. Chem.* **1980,** *52,* 669. (b) Negishi, E. I. *Acc. Chem. Res.* **1982,** *15,* 340. (c) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 508.

(2) For reviews, see: (a) Heck, R. F. *Acc. Chem. Res.* **1979,** *12,* 146. (b) Heck, R. F. *Organic Reactions (N.Y.)* **1982,** *27,* 345. (c) Heck, R. F. *Palladium in Organic Synthesis;* Academic Press, New York, 1985.

(3) All the steps of these catalytic mechanisms have been validated independently and characterized kinetically (see, e.g., refs 1, 2, and 4). Yet, to the best of our knowledge, no study of the kinetics of a whole catalytic sequence has been achieved so far for palladium (compare, e.g., ref 5 for nickel catalysis). This makes it difficult to decide which step is the rate-determining step (rds) of these processes. However, the nucleophilic attack (eq 2)[4a-d] or the olefin addition (eq 3) appears to be almost insensitive to the nature (X = Cl, Br, I) of the halide substituent of the activated aromatic halide. On the other hand, the rate of oxidative addition (eq 1) is extremely susceptible to the nature of X (ArI > ArBr $\gg$ ArCl),[1,2,4a-d,6] as is often the case for the overall efficiency of the catalysis; we are thus enclined to consider that, for such cases, the rds consists generally in the oxidative addition in eq 1.

(4) (i) For oxidative addition as the rds, see: (a) Fauvarque, J. F.; Jutand, A. *Bull. Soc. Chim. Fr.* **1976,** 765. (b) Fauvarque, J. F.; Jutand, A. *J. Organomet. Chem.* **1977,** *132,* C17. (c) Fauvarque, J. F.; Jutand, A. *J. Organomet. Chem.* **1979,** *177,* 273. (d) Fauvarque, J. F.; Jutand, A. *J. Organomet. Chem.* **1981,** *209,* 109. For substitution as the rds, see: (e) Negishi, E.; Takahashi, T.; Baba, S.; van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987,** *109,* 2393. (ii) For reductive elimination as the rds, see: (f) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980,** *102,* 4933. (g) Loar, M.; Stille, J. K. *J. Am. Chem. Soc.* **1981,** *103,* 4174. (h) Moravsky, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981,** *103,* 4182. (i) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981,** *54,* 1868. (j) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984,** *106,* 8181.

(5) (a) Amatore, C.; Jutand, A. *Organometallics* **1988,** *7,* 2203. (b) Amatore, C.; Jutand, A. *J. Am. Chem. Soc.* **1991,** *113,* 2819. (c) Amatore, C.; Jutand, A.; Mottier, L. *J. Electroanal. Chem.* **1991,** *306,* 125. (d) Amatore, C.; Jutand, A. *J. Electroanal. Chem.* **1991,** *306,* 141.

(6) See e.g.: (a) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971,** *28,* 287. (b) Coulson, D. R. *J. Chem. Soc., Chem. Commun.* **1968,** 1530.

(7) (a) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1975,** 1673. (b) Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1975,** *12,* 187.

(8) (a) Fauvarque, J. F.; Pflüger, F.; Troupel, M. *J. Organomet. Chem.* **1981,** *208,* 419. (b) Amatore, C.; Pflüger, F. *Organometallics* **1990,** *9,* 2276. For identical rate laws and interpretations in oxidative additions to Ni^0(PR$_3$)$_4$, see: (c) Elson, I. E.; Morrell, D. G.; Kochi, J. K. *J. Organomet. Chem.* **1975,** *84,* C7. (d) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979,** *101,* 6319.

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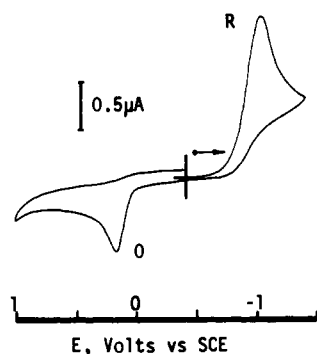
Figure 1. Cyclic voltammetry of $Pd^{II}(PPh_3)_2Cl_2$, 2 mM, in THF/0.3 M *n*-Bu_4NBF_4 in the presence of 1 equiv of PPh_3, at a gold disk electrode (diameter 0.5 mm). $v = 0.2$ V s^{-1}, 20 °C.

consists in decreasing the effect of the ligand dissociation equilibria by introducing the catalyst in the medium in a poorly ligated form $Pd^0(PR_3)_2L_2$ (or Pd^0L_4 in the presence of 2 equiv of phosphine), where L is a ligand more easily removed from palladium than PR_3. Several examples of this approach have been reported in the literature,[10,11] with L_n being, e.g., olefins, COT, dba, etc. A second, and more drastic, approach consists in bypassing totally the two ligand dissociation equilibria by generating in situ the zerovalent palladium in its low-ligated active form $Pd^0(PR_3)_2$. This can be achieved by chemical reduction[12,13] of a divalent precursor, e.g., $Pd^{II}(PR_3)_2Cl_2$ or $Pd^{II}(OAc)_2$ in presence of the required amount of phosphine.[14]

The resulting increase in the rates of oxidative addition is well illustrated by the fact that, e.g., $Pd^0(PCy_3)_2(dba)$, generated in situ from $Pd^0(dba)_2$ and 2 equiv of tricyclohexylphosphine,[10b] is able to activate chlorobenzene. On the other hand, this enhancement of reactivity makes difficult a quantitative determination of the corresponding kinetics by classical means. We therefore developed an electrochemical approach to this problem.

(9) In the absence of added phosphine, one usually reports an apparent rate constant of oxidative addition, k_{ap}, which corresponds to a reformulation of eq 5 as follows:

$$d[Pd^0]/dt = d[ArX]/dt = -k_{ap}[Pd^0][ArX] \qquad (5')$$

with

$$k_{ap} = k_{mes}/[PPh_3] = k_{true}(K_2/[PPh_3]) \ll k_{true} \qquad (9)$$

k_{ap} is considerably smaller than k_{true}, because only a considerably small fraction (viz., of the order of $(K_2/[PPh_3]) \ll 1$) of the palladium "catalyst" introduced in the reaction medium is under the active catalytic form Pd^0-$(PPh_3)_2$.

(10) See e.g.: (a) Brown, J. M.; Cooley, N. A. *Organometallics* **1990**, *9*, 353. (b) Huser, M. T.; Youinou, M. T.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1386. (c) Fiaud, J. C.; Hibon de Gournay, A.; Larchevêque, M.; Kagan, H. B. *J. Organomet. Chem.* **1978**, *154*, 175. (d) Genet, J. P.; Jugé, S.; Ruis Montès, J.; Gaudin, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 718.

(11) See also ref 2. In the Heck reaction, palladium is generally introduced as a divalent complex, e.g., $Pd(OAc)_2$, which is reduced in the reaction medium.

(12) For Nu⁻ as the reducing agent, see e.g.: (a) ref 4a. (b) Hayashi, T.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, 1871. (c) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992. (d) Minato, A.; Tamao, K.; Hayashi, T.; Suzuki, K.; Kumada, M. *Tetrahedron Lett.* **1980**, 845. (e) Minato, A.; Tamao, K.; Hayashi, T.; Suzuki, K.; Kumada, M. *Tetrahedron Lett.* **1981**, 5319. (f) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higushi; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158. (g) Uno, M.; Seto, K.; Ueda, W.; Masuda, M.; Takahashi, S. *Synthesis* **1985**, 506.

(13) For reduction by an organometal, see e.g.: (a) Kosugi, M.; Shimizu, T.; Migita, T. *Chem. Lett.* **1978**, 13. (b) King, A. O.; Negishi, E. I.; Villani, F. J.; Silveria, A., Jr. *J. Org. Chem.* **1978**, *43*, 358. (c) Negishi, E. I.; Okukado, N.; King, A. O.; van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254. (d) Urata, H.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *J. Organomet. Chem.* **1989**, *364*, 235.

(14) Another interesting approach consists in introducing the transition-metal catalyst under the form of the σ-aryl derivative $ArPd^{II}L_2X$ formed independently (eq 1). Compare, e.g., refs 4c and 12c and Sekiya, A.; Ishikawa, N. *J. Organomet. Chem.* **1976**, *118*, 349.

Indeed we could establish that the transient or preparative electrochemical reduction of $Pd^{II}(PPh_3)_2X_2$, where X = Cl, Br, or I, is a two-electron process affording, in the absence of added phosphine, a low-ligated zerovalent palladium "$Pd^0(PPh_3)_2$":[13d,15,16]

$$Pd^{II}(PPh_3)_2X_2 + 2e \rightarrow Pd^0(PPh_3)_2 \qquad (10)$$
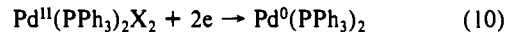
The zerovalent nature of the electrogenerated palladium complex in eq 10 has been further established by its rapid decay in the presence of PhI,[17] and ^{31}P NMR characterization of the *trans*-$PhPd^{II}(PPh_3)_2I$ as the final product of the reaction

$$Pd^0(PPh_3)_2 + PhI \rightarrow PhPd^{II}(PPh_3)_2I \qquad (11)$$

The electrogenerated zerovalent palladium is oxidizable in cyclic voltammetry (see wave O in Table I). This enabled us to use cyclic voltammetry to follow the kinetics of its reaction with PhI (eq 11).[15] This led to a puzzling observation. Indeed, the half-life of the electrogenerated $Pd^0(PPh_3)_2$ in the presence of PhI (eq 11) depends on the nature of the divalent palladium precursor used (i.e., X = Cl or Br in eq 10). Moreover (vide infra) this half-life is independent of the initial palladium concentration when X = Br, whereas it depends on the palladium concentration when X = Cl. Such results strongly suggest that the halide ions supposedly electrogenerated with $Pd^0(PPh_3)_2$ in eq 10 are not "inert" ions but play a significant role on the nature, and therefore on the reactivity, of the low-ligated zerovalent palladium.

These kinetic observations agree with a previous contribution by Negishi et al.[16] Indeed, in this seminal work, these researchers reported that reduction of $Pd^{II}(PPh_3)_2X_2$ (X = Cl, Br, or I) with 2 equiv of RLi affords a different ^{31}P NMR signal for each halide. On the basis of ^{31}P NMR data, they concluded that the only possible structure for $Pd^0(PPh_3)_2$ generated under these conditions was $LiXPd^0(PPh_3)_2$, or $Li_2X_2Pd^0(PPh_3)_2$ or aggregates thereof.[16] This spectroscopic observation was further confirmed[15] by the evolution of the ^{31}P NMR spectrum of an electrolyzed solution of $Pd^{II}(PPh_3)_2Cl_2$, 16 mM in THF/0.2 M *n*-Bu_4NBF_4, as a function of the chloride ion concentration. When electrolysis was performed in the absence of purposely added chloride ions, three signals[17,18] were observed at 23.15, 25.22, and 27.14 ppm relative to H_3PO_4 (162 MHz, THF) with relative integrations 1/0.7/0.6. When the same electrolysis was performed in the presence of 6 equiv of *n*-Bu_4NCl, only one signal at 22.98 ppm was observed.

Moreover, coordination of zerovalent palladium catalyst by halide ions has also been invoked to explain the larger yields obtained in palladium-catalyzed nucleophilic substitutions of aryl and vinyl triflates,[19] in the presence of halide ions. There are also several other reports in the literature, e.g., about the Heck reaction,[20] where the presence of halide ions appears crucial to the

(15) Amatore, C.; Azzabi, M.; Jutand, A. *J. Organomet. Chem.* **1989**, *363*, C41.

(16) Negishi, E. 1.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1338.

(17) The chemical shifts observed in the ^{31}P NMR of an electrolyzed solution of $Pd^{II}(PPh_3)_2X_2$ (X = Cl or Br) are consistent with those reported previously by Negishi et al.[16] for $Pd^0(PPh_3)_2$ generated by chemical reduction of $Pd^{II}(PPh_3)_2X_2$ by 2 equiv of RLi (however, see footnote 18 for important differences).

(18) In ref 16, Negishi et al. report a single ^{31}P NMR signal for each case X = Cl, Br, or I. In our case, we obtain three (X = Cl) or two (X = Br) signals. We ascribe this difference to the difference in concentrations (vide infra), and possibly to the role of Li$^+$ generated upon chemical reduction, rather than to an intrinsic difference between electrochemical and chemical reductions (vide infra).
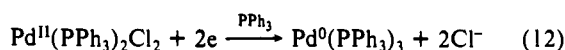
(19) (a) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (b) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. (c) Andersson, C. M.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 2112. (d) Friess, B.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1988**, *29*, 4089. (e) Karabellas, K.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1773. (f) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron Lett.* **1989**, *30*, 2581. (g) Arcadi, A.; Cacchi, S.; Marinelli, F.; Morera, E.; Ortar, G. *Tetrahedron* **1990**, *46*, 7151.

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success of the reaction,[21] whenever the divalent palladium precursor complex bears poorly donating ligands.

This prompted us to undertake a detailed kinetic analysis of the reactivity of the low-ligated zerovalent palladium $Pd^0(PPh_3)_2$ as a function of the nature and concentration of chloride and bromide ions.[22] We present and discuss hereafter the results of this kinetic study.

Results

Rate and Mechanism of Oxidative Addition of PhI to Electrogenerated Zerovalent Palladium in the Presence of PPh_3.
Figure 1 represents the cyclic voltammetry of the reduction of Pd^{II}-$(PPh_3)_2Cl_2$, 2 mM in THF/0.3 M n-Bu$_4$NBF$_4$, at 0.2 V s^{-1}, in the presence of 1 equiv of PPh_3. A two-electron, chemically irreversible reduction wave, R (see Table I), is observed during the cathodic scan.[23] Upon scan inversion, an oxidation wave, O ($E^p = 0.10$ V vs SCE at 0.2 V s^{-1}), is observed. This wave is identical with that due to oxidation of $Pd^0(PPh_3)_4$ in the presence of 2 equiv of n-Bu$_4$NCl.[24] The production of $Pd^0(PPh_3)_3$ upon reduction at wave R

$$Pd^{II}(PPh_3)_2Cl_2 + 2e \xrightarrow{PPh_3} Pd^0(PPh_3)_3 + 2Cl^- \quad (12)$$

is quantitative, as established hereafter by double-step chro-

log(θ |PhI|/|PPh₃|)

Figure 2. Chronoamperometry of $Pd^{II}(PPh_3)_2Cl_2$ (0.5 mM $\leq C^0 \leq 2$ mM) in THF/0.3 M n-Bu$_4$NBF$_4$ in the presence of PPh_3 (1–5 equiv) and PhI (5–50 equiv), at a gold disk electrode (diameter 0.5 and 0.125 mm). Variations of $R(\theta)$, defined in eq 13, as a function of the unifying kinetic parameter $\theta[PhI]/[PPh_3]$; θ, s; [PhI] and [PPh$_3$], M; 20 °C. Solid line: theoretical variations for the rate law in eq 5 with $k_{mes} = 6.5 \times 10^{-2}$ s^{-1}.

log (|PhI|/v)
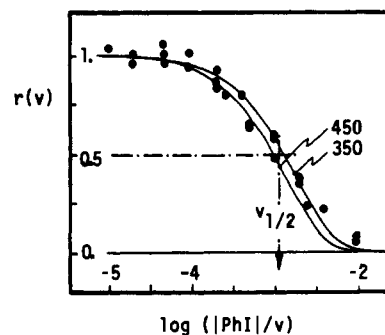
Figure 3. Cyclic voltammetry of $Pd^{II}(PPh_3)_2Br_2$ (0.5 mM $\leq C^0 \leq 2$ mM) in THF/0.3 M n-Bu$_4$NBF$_4$ in the presence of PhI (1–10 equiv), at a gold disk electrode (diameter 0.5 and 0.125 mm). Variations of $r(v)$, defined in eq 14, as a function of the unifying kinetic parameter [PhI]/v; [PhI], M; v, V s^{-1}; 20 °C. Solid lines: theoretical variations for the rate law in eq 16 with $k = 350$ M^{-1} s^{-1} or $k = 450$ M^{-1} s^{-1} (compare to $k = 405 \pm 90$ M^{-1} s^{-1} predicted for these conditions with eq 22 with $k_B = (5 \pm 1) \times 10^2$ M^{-1} s^{-1}, $k_C = 50 \pm 5$ M^{-1} s^{-1}, and $K_{BC} = 90 \pm 5$ M^{-1}; see text).
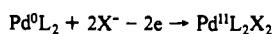
(20) (a) Jeffery, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1287. (b) Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667. (c) Grigg, R.; Sridharan, B.; Stevenson, P.; Worakun, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1697. (d) Jeffery, T. *Synthesis* **1987**, 70. (e) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1987**, *28*, 3039. (f) Larock, R. C.; Babu, S. *Tetrahedron Lett.* **1987**, *28*, 5291. (g) Larock, R. C.; Baker, B. E. *Tetrahedron Lett.* **1988**, *29*, 905. (h) Larock, R. C.; Song, H.; Baker, B. E.; Gong, W. H. *Tetrahedron Lett.* **1988**, *29*, 2919. (i) Larock, R. C.; Stinn, D. E. *Tetrahedron Lett.* **1988**, *29*, 4687. (j) Grigg, R.; Stevenson, P.; Worakun, T. *Tetrahedron* **1988**, *44*, 2033. (k) Grigg, R.; Stevenson, P.; Worakun, T. *Tetrahedron* **1988**, *44*, 2049. (l) Burns, B.; Grigg, R.; Sridharan, V.; Worakun, T. *Tetrahedron Lett.* **1988**, *29*, 4325. (m) Burns, B.; Grigg, R.; Ratananukui, P.; Sridharan, V.; Stevenson, P.; Worakun, T. *Tetrahedron Lett.* **1988**, *29*, 4329. (n) Jeffery, T. *Synth. Commun.* **1988**, *18*, 77. (o) Larock, R. C.; Johnson, P. L. *J. Chem. Soc., Chem. Commun.* **1989**, *18*, 1368. (p) Hoffmann, H. M. R.; Schmidt, B.; Wolff, S. *Tetrahedron* **1989**, *45*, 6113. (q) Larock, R. C.; Gong, W. H.; Baker, B. E. *Tetrahedron Lett.* **1989**, *30*, 2603. (r) Amorese, A.; Arcadi, A.; Bernocchi, E.; Cacchi, S.; Cerrini, S.; Fedeli, W.; Ortar, G. *Tetrahedron* **1989**, *45*, 813. (s) Grigg, R.; Sridharan, V.; Stevenson, P.; Sukirthalingam, S. *Tetrahedron* **1989**, *45*, 3557. (t) Carlström, A. S.; Frejd, T. *Synthesis* **1989**, 414. (u) Larock, R. C.; Berrios-Pena, N.; Narayanan, K. *J. Org. Chem.* **1990**, *55*, 3447. (v) Larock, R. C.; Fried, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 5882. (w) Lawsky, A.; Reiser, O.; de Meijere, A. *Synlett* **1990**, 405. (x) Andersson, C. M.; Larsson, J.; Hallberg, A. *J. Org. Chem.* **1990**, *55*, 5757.

(21) Tetraalkylammonium halides were used originally as phase-transfer catalysts.[20a] However, it appears now that their role, although not yet elucidated, cannot always be rationalized on such a basis: Cacchi, S. Communication presented at the *EUCHEM Conference on Palladium in Organic Synthesis*, Sigtuna, Sweden, August 1990.
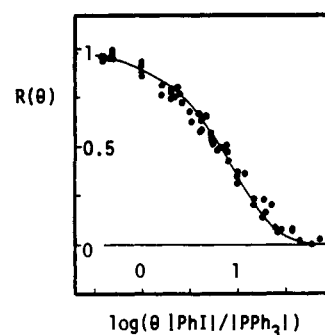
(22) The effect of iodide ions could not be investigated by the method presented hereafter, since their oxidation wave interferes with that of Pd^0-$(PPh_3)_2$ (wave O in Figure 4).

(23) Amatore, C.; Azzabi, M.; Calas, P.; Jutand, A.; Lefrou, C.; Rollin, Y. *J. Electroanal. Chem.* **1990**, *288*, 45.

(24) (a) The $Pd^0(PPh_3)_4$ (i.e., $Pd^0(PPh_3)_3$, which is the main species present in solution)[7] oxidation wave potential depends on the halide ion concentration. For example, at 0.2 V s^{-1}, $Pd^0(PPh_3)_4$ is oxidized at $E^p = 0.34_0$ V vs SCE in the absence of halide ions, and at 0.04_0 V vs SCE in the presence of 200 mM n-Bu$_4$NCl. (b) The oxidation peak of electrogenerated zerovalent palladium is extremely dependent on the halide ion concentration (compare, e.g., Figure 4); yet it involves always a two-electron consumption. (c) We ascribe the behaviors in (a) or (b) to the participation of free halide ions in the oxidation

$$Pd^0L_2 + 2X^- - 2e \rightarrow Pd^{II}L_2X_2$$

via complex antecedent or follow-up reactions,[25] as well as to a change of nature of "Pd^0L_2" (vide infra and footnote 26). Indeed if the scan is reversed toward negative potentials after scanning over wave O, one can detect in addition to wave R (due to the reduction of $Pd^{II}L_2X_2$ regenerated by diffusion)[25] a new reduction wave R' (e.g., $E^p \approx -0.27$ V vs SCE at 0.2 V s^{-1}, in THF, X = Br) positive of wave R. The peak potential of wave R' is extremely solvent dependent (THF, DMF, ACN) (Amatore, C.; Jutand, A.; Nielsen, M. F. Unpublished results). Also, in the presence of an excess of halide ion (Cl$^-$ or Br$^-$), this wave disappears and the system of two waves O and R behaves as a quasi-reversible system.[25] We therefore ascribe wave R' to the reduction of a cationic intermediate, $Pd^{II}L_2X_x^{(2-x)+}$ with $x < 2$, possibly coordinated by the solvent.

noamperometry.[25] Thus, a first potential step is performed on the plateau of wave R; after a time θ has elapsed, the potential is set at a constant value on the plateau of wave O for an identical duration θ. The ratio between the anodic current at time 2θ and the cathodic current at time θ is then determined. Its value, $[i_a/i_c]_{(\theta)} = 0.295 \pm 0.05$, is constant (1 ms $\leq \theta \leq 100$ ms) and equal to that, 0.293,[25,27] expected for a reversible process. This establishes that $Pd^0(PPh_3)_3$ is formed stoichiometrically at wave R (eq 12) and reoxidized quantitatively at wave O.

In the presence of PhI, wave R remains unchanged, but wave O disappears, indicating the occurrence of the fast oxidative addition of PhI to the electrogenerated $Pd^0(PPh_3)_3$. Wave O is restored upon increasing the scan rate, i.e., upon decreasing the time allowed for reaction between PhI and $Pd^0(PPh_3)_3$.[25,27] The kinetics of this reaction is best monitored by using double-step chronoamperometry. Via the above procedure, $[i_a/i_c]$ is now determined as a function of θ, [PPh$_3$], and [PhI] and normalized

(25) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980. (b) Andrieux, C. P.; Savéant, J. M. In *Investigation of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. 6, 4/E, Part 2, pp 305–390.

(26) In particular, this establishes that a maximum concentration of 4 mM of chloride ions, resulting from the production of 2 equiv of Cl$^-$ during the reduction in eq 12, does not affect the coordination equilibria of $Pd^0(PPh_3)_3$ under these conditions (however, vide infra for larger chloride ion concentrations). Therefore, the potential shift of wave O in the presence of small excesses of Cl$^-$ (compare footnote 24) results from kinetic phenomena in the near vicinity of the electrode, rather than from structural variations of the bulk zerovalent palladium complex.

(27) (a) Hanafey, M. K.; Scott, R. L.; Ridgway, T. H.; Reilley, C. N. *Anal. Chem.* **1978**, *50*, 116. (b) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1980**, *107*, 353. (c) Amatore, C.; Kuchynka, D. J.; Kochi, J. K. *J. Electroanal. Chem.* **1988**, *241*, 181. (d) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 1670.

to that obtained in the absence of PhI. Thus

$$R(\theta) = [i_a/i_c]_{(\theta)}/0.293 \qquad (13)$$

represents the fraction of the electrogenerated zerovalent palladium that has not reacted with PhI during the time θ.[27] Variations of $R(\theta)$ as a function of θ for different concentrations of PhI or PPh$_3$ are represented in Figure 2. It is seen that $R(\theta)$ depends on a single kinetic parameter, $\{\theta[PhI]/[PPh_3]\}$,[27b-d,28] which establishes that the disappearance of the electrogenerated zerovalent palladium obeys the rate law in eq 5. Fitting the experimental data in Figure 2 to the working curve[27] (solid line in Figure 2) derived from eq 5 allows one to determine $k_{mes} = (6.5 \pm 0.5) \times 10^{-2}$ s^{-1}, for the rate of the overall oxidative addition (eq 5) under our conditions, at 20 °C. The latter is identical, within the experimental accuracy, with that, $(5.9 \pm 0.2) \times 10^{-2}$ s^{-1}, determined independently by monitoring the homogeneous reaction between Pd^0(PPh$_3$)$_4$ and PhI in the presence of excess PPh$_3$ at 20 °C.[8a] This identity establishes that the electrogenerated zerovalent palladium species are identical with those involved in homogeneous experiments, i.e. that electrochemical conditions do not introduce any artifact in the determination of the rates of oxidative addition.[26]

Rate and Mechanism of Oxidative Addition of PhI to Electrogenerated Zerovalent Palladium in the Absence of PPh$_3$. In the absence of added phosphine, the cyclic voltammetry of Pd^{II}-(PPh$_3$)$_2$X$_2$, X = Cl,[15] Br, or I, is basically identical with that represented in Figure 1, except for the expected slight variations of the peak potentials of waves R or O (compare Table I). In all cases, waves R and O correspond to two-electron processes,[23] showing that the electron stoichiometry in eq 12 is retained independently of the absence of PPh$_3$ or of the nature of the halide.

The kinetics of oxidative addition of PhI to the electrogenerated zerovalent palladium can then be determined from the variations of the ratio, $r(v)$, of the current peak i^p_O of wave O in the presence of PhI to that, $(i^p_O)_0$, measured at the same scan rate, v, in the absence of PhI:

$$r(v) = i^p_O/(i^p_O)_0 \qquad (14)$$

As $R(\theta)$ in eq 13,[29] the value of this ratio is directly related to the fraction of zerovalent palladium that has not reacted with PhI during the time required for scanning the potential between wave R and wave O.

When Pd^0(PPh$_3$)$_2$ is electrogenerated from Pd^{II}(PPh$_3$)$_2$Cl$_2$, $r(v)$ is a function of a single kinetic parameter $\{[Pd^{II}(PPh_3)_2Cl_2]-[PhI]/v\}$.[15,28] This corresponds[28] to a reaction second order in electrogenerated zerovalent palladium and first order in PhI (vide infra for the origin of such a "trimolecular" rate law):

$$d[Pd^0]/dt = -k[Pd^0]^2[PhI] \qquad (15)$$

When Pd^0(PPh$_3$)$_2$ is electrogenerated from Pd^{II}(PPh$_3$)$_2$Br$_2$, $r(v)$ is a function of a single parameter $\{[PhI]/v\}$, as shown in Figure 3, and is independent of the palladium concentration. This corresponds[28] to a rate law first order in electrogenerated zerovalent palladium and first order in PhI:

$$d[Pd^0]/dt = -k[Pd^0][PhI] \qquad (16)$$

The discrepancy between the rate laws in eqs 15 and 16 is not related to a change in the nature of the overall reaction between the electrogenerated zerovalent palladium with PhI, since in both cases preparative electrolysis demonstrates that the product of
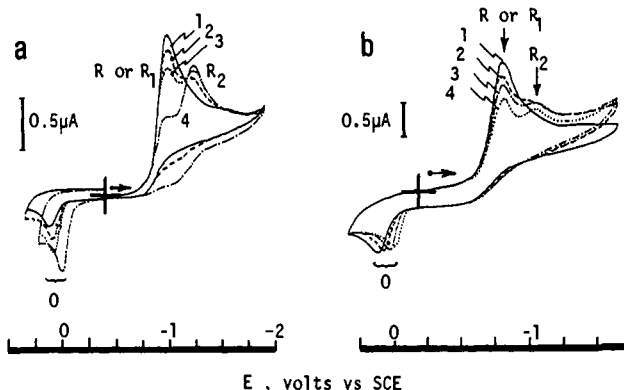
Figure 4. Cyclic voltammetry of (a) Pd^{II}(PPh$_3$)$_2$Cl$_2$, 2 mM, or (b) Pd^{II}(PPh$_3$)$_2$Br$_2$, 2 mM, in THF/0.3 M n-Bu$_4$NBF$_4$ at a gold disk electrode (diameter 0.5 mm), as a function of the concentration of added n-Bu$_4$NCl (a) or n-Bu$_4$NBr (b). (a) [n-Bu$_4$NCl] = 0 (1), 0.01 (2), 0.03 (3), and 0.21 M (4). (b) [n-Bu$_4$NBr] = 0 (1), 0.07 (2), 0.15 (3), and 0.19 M (4). $v = 0.2$ V s^{-1}, 20 °C.

the reaction is the *trans*-phenylpalladium(II) derivative PhPd^{II}-(PPh$_3$)$_2$I. The difference observed is then only indicative of a change in the intimate mechanism of the oxidative addition, and therefore of a difference in the nature of the electrogenerated zerovalent palladium species. Such an ad hoc interpretation is further confirmed by the observation of two signals (22.30 and 24.49 ppm with relative integration 1/0.65)[16] in the ^{31}P NMR spectrum of an electrolyzed solution of Pd^{II}(PPh$_3$)$_2$Br$_2$ (16 mM, no added bromide ions) under conditions identical with those used above for Pd^{II}(PPh$_3$)$_2$Cl$_2$.

Since these differences can only be due to the nature of the halide (X = Cl or Br) initially present in the parent divalent palladium Pd^{II}(PPh$_3$)$_2$X$_2$, we want to examine in detail the effect of purposely added chloride or bromide ions on the rate and mechanism of oxidative addition of PhI to electrogenerated zerovalent palladium.

Rate and Mechanism of Oxidative Addition of PhI to Electrogenerated Zerovalent Palladium in the Presence of Chloride or Bromide Ions. In order to avoid any interference of a possible competition between different halide ions present in the medium, this study was performed by using Pd^{II}(PPh$_3$)$_2$Cl$_2$ (respectively Pd^{II}(PPh$_3$)$_2$Br$_2$), as the divalent palladium precursor in the study dealing with the effect of chloride (respectively bromide) ions. Halide ions were introduced under the form of a known concentration of n-Bu$_4$NCl (respectively n-Bu$_4$NBr), which was supposed to be totally dissociated in the medium. Figure 4 illustrates the distortions of the cyclic voltammetry of Pd^{II}(PPh$_3$)$_2$Cl$_2$ (respectively Pd^{II}(PPh$_3$)$_2$Br$_2$) as a function of the excess of n-Bu$_4$NCl[15] (respectively n-Bu$_4$NBr). The main observation is that in either case the initial two-electron wave R splits into two halide-dependent successive one-electron waves R$_1$ and R$_2$ (see Table I),[30] which emphasizes the stabilization of monovalent palladium species by halide ions.[31] Noteworthy, the stabilization of monovalent palladium species by bromide ions is smaller than by chloride ions, as evidenced by the fact that, in Figure 4b, the splitting of the initial two-electron wave R into two one-electron waves (R$_1$ and R$_2$) is incomplete even at large concentrations of n-Bu$_4$NBr (compare Figure 4a).
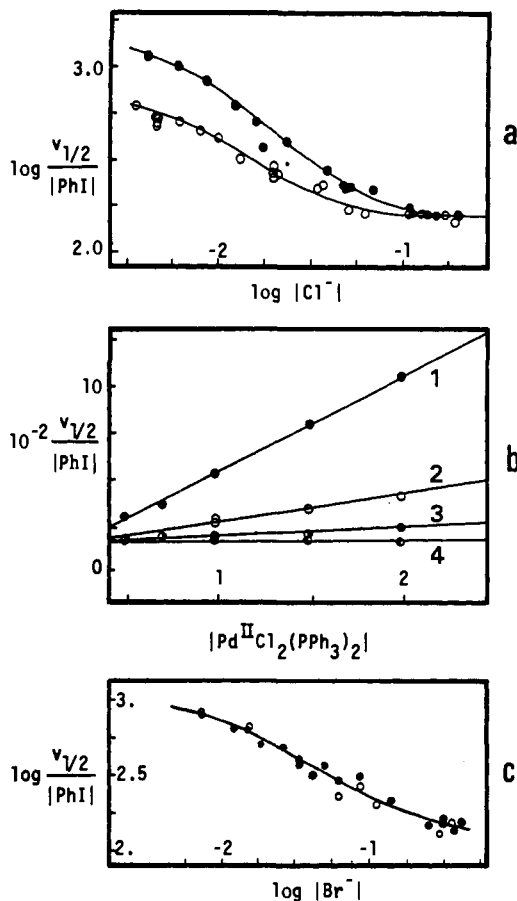
Wave O is also affected by the presence of halide ions, yet only in its shape and peak location.[32] For a given excess of n-Bu$_4$NX,

(28) (a) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1983**, *144*, 59. (b) Amatore, C. In *Organic Electrochemistry*, 3rd ed.; Lund, H., Baizer, M., Eds.; Dekker: New York, 1991; Chapter 2, pp 11–119.

(29) A study by double-step chronoamperometry[27] (compare preceding section) would have been preferable from the point of view of precision and ease of theoretical treatment of the data (see, e.g., Experimental Section). However, for this study, we favored cyclic voltammetry, since it allowed a simultaneous characterization of the system of waves at hand, particularly in order to avoid the interference with the oxidation waves of electrogenerated or added halide ions.

(30) The electron consumptions at waves R$_1$ and R$_2$ were determined by comparing their current peaks to that of wave R, which was shown independently to feature a two-electron process.[23]

(31) In the absence of excess halide ions, monovalent palladium species must be reducible at a potential positive to that of wave R, in order to account for an overall two-electron process at wave R. See ref 27b and (a) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1977**, *85*, 27. (b) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1979**, *102*, 21. (c) Amatore, C.; Lexa, D.; Savéant, J. M. *J. Electroanal. Chem.* **1980**, *111*, 81. (d) Amatore, C.; Gareil, M.; Savéant, J. M. *J. Electroanal. Chem.* **1983**, *147*, 1.

Figure 6. Oxidative addition of para-substituted iodobenzenes to Pd^0-$(PPh_3)_4$, 2 mM, in $THF/0.3$ M $n\text{-}Bu_4NBF_4$. (a) Arrhenius plot[35] for reaction with C_6H_5I; $k_{ap}{}^H$, M^{-1} s^{-1}. (b) Hammett plot for a series of para-substituted iodobenzenes, $p\text{-}IC_6H_4Z$, at 20 °C. Z: NO_2 (1), CN (2), MeCO (3), Cl (4), Br (5), H (6), Me (7), MeO (8), OH (9). Regression line: $\log (k_{ap}/k_{ap}{}^H) = 0.20 + 2.7 \sigma$; correlation coefficient 0.985 (data for $p\text{-}IC_6H_4CO_2H$ was excluded).

Figure 5. Oxidative addition of PhI to electrogenerated zerovalent palladium species, 20 °C. (a) Variations of $v_{1/2}$ for $[Pd^{II}(PPh_3)_2Cl_2] = 1$ (O) and 2 mM (●); solid lines are the theoretical predictions according to eq 21 with $K_{BC} = 70$ M^{-1}, $k_A K_{BA} = 9 \times 10^5$ M^{-1} s^{-1}, $k_B = 0$ M^{-1} s^{-1}, and $k_C = 72$ M^{-1} s^{-1}. (b) Variations of $v_{1/2}$ as a function of $[Pd^{II}\text{-}(PPh_3)_2Cl_2]$ for $[n\text{-}Bu_4NCl] = 3$ (1), 20 (2), 50 (3), and 110 mM (4); $[Pd^{II}(PPh_3)_2Cl_2]$, mM. (c) Variations of $v_{1/2}$ for $[Pd^{II}(PPh_3)_2Br_2] = 1$ (O) and 2 mM (●); solid line is the theoretical prediction according to eq 22 with $K_{BC} = 90$ M^{-1}, $k_B = 500$ M^{-1} s^{-1}, and $k_C = 50$ M^{-1} s^{-1}. In (a), (b), and (c), $v_{1/2}$, V s^{-1}; [PhI], [Cl⁻], or [Br⁻], M.

$X = Cl$ or Br, the kinetics of oxidative addition of PhI to the zerovalent palladium electrogenerated upon reduction at wave R_2 can therefore be monitored[29] as above by the variations of $r(v)$ in eq 14 as a function of scan rate and $Pd^{II}(PPh_3)_2X_2$ and PhI concentrations.
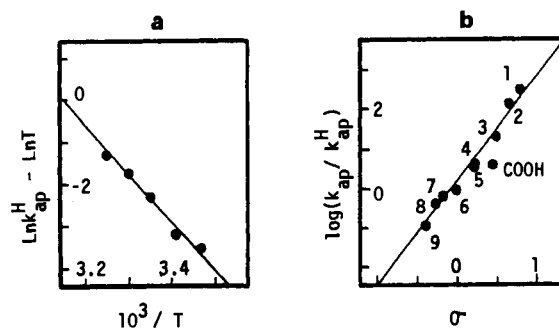
To simplify the presentation and analysis of these results, we will focus in the following on the variations of $v_{1/2}$ with $n\text{-}Bu_4NX$, $X = Cl$ or Br, and $Pd^{II}(PPh_3)_2X_2$ and PhI concentrations, $v_{1/2}$ being the scan rate such as $r(v_{1/2}) = 0.5$ (see Figure 3) for a particular set of these concentrations. Indeed this variable is related to the half-life, $t_{1/2}$, of the electrogenerated zerovalent palladium under the specific conditions considered (see Experimental Section).[28] Under any of these conditions, $v_{1/2}$ is found to be strictly proportional to the concentration of PhI, which demonstrates[28,33] that the rate law of oxidative addition is first

order in PhI, irrespective of the palladium or halide ion concentrations. However, the reaction orders pertaining to palladium or halide ion are variable and greatly dependent on these concentrations as well as on the nature of the halide ion. This is illustrated for chloride ions by Figure 5a, which presents the variations of $v_{1/2}$ with the chloride ion concentrations, and Figure 5b, which gives the dependence of $v_{1/2}$ with the $Pd^{II}(PPh_3)_2Cl_2$ concentration at different concentrations of chloride ion. Thus, a negative order (between 0 and −1) in chloride ion and a positive order (between 1 and 2) in zerovalent palladium are observed,[28,33] indicating a complex rate law. A similar behavior is observed for bromide ions (Figure 5c), yet with the important difference that the reaction remains first order in zerovalent palladium, $v_{1/2}$ being independent of the palladium concentration.

Since it has been checked by preparative scale electrolysis that the product of the reaction is $PhPd^{II}(PPh_3)_2I$, irrespective of the exact above experimental conditions ($X = Cl$ or Br), these variations only reflect the great dependence of the mechanism of oxidative addition on the halide ion nature and concentration.

Oxidative Addition of PhI to $Pd^0(PPh_3)_4$ in the Presence of Chloride Ions. On the basis of the mechanism of oxidative addition to saturated zerovalent palladium (eqs 4, 6, and 7),[8a,b] $Pd^0(PPh_3)_2$ is formed, at least as a transient intermediate. Owing to the above results, which point to a strong interaction between halide ions and low-ligated zerovalent species, one expects halide ions to affect the mechanism of the oxidative addition to $Pd^0(PPh_3)_4$, via possible interactions with the transient $Pd^0(PPh_3)_2$. To examine the occurrence of such interactions, we examined this reaction in the presence of an excess of chloride ions.

^{31}P NMR of a solution of $Pd^0(PPh_3)_4$, 16 mM in THF at room temperature, shows a broad signal at 13.41 ppm vs H_3PO_4. When 25 equiv of $n\text{-}Bu_4NCl$ are added to this solution, this signal is replaced by a new broad signal at 9.68 ppm. This suffices to establish that the presence of an excess of chloride ions affects the dissociation equilibria in eqs 4 and 6. This observation is further confirmed by the negative shift of the oxidation potential ($E_{1/2} = 0.34$ and 0.04 V vs SCE, at 0.2 V s^{-1}, respectively, in the absence and in the presence of 200 mM $n\text{-}Bu_4NCl$) of $Pd^0(PPh_3)_4$, 2 mM, in the presence of an excess of chloride ions.[24,26]

A systematic kinetic study of oxidative additions of a series of iodobenzenes to $Pd^0(PPh_3)_4$ in THF has been reported previously.[8a] It was found that the rate constant of the overall reaction follows a Hammett correlation with $\rho = 2.0$, and that the activation parameters of the oxidative addition of PhI were $\Delta H^{\ddagger} = 77$ kJ mol^{-1} and $\Delta S^{\ddagger} = 13$ J mol^{-1} K^{-1}. In order to compare these results to those obtained in the presence of an excess of chloride ions, we used an identical method for determining the kinetics of oxidative addition. Thus, the time dependence of the concentration of $Pd^0(PPh_3)_4$ in the presence of a series of para-substituted iodobenzenes was monitored by using the variations of the current plateau, $i_{ox}{}^{lim}$, of the oxidation wave of $Pd^0(PPh_3)_4$ observed at a rotating disk electrode.[8a] For, e.g., a solution of PhI, 2 mM,

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(32) The electron consumption at wave O remains constant (2e), as established by double-step chronoamperometry. Thus, over the whole range of chloride ion concentration considered in this study, $R(\theta)$ in eq 13 remained unity within the experimental accuracy (5%). The increase of current peak of wave O in Figure 4 then results merely from variations in diffusion coefficients and/or kinetics of electron transfer, suggesting a structural change of the electroactive species upon change of the chloride ion concentration (vide infra).

(33) For a situation of the kind considered here, and assuming an overall rate law:

$$d[Pd^0]/dt = -k[Pd^0]^p[PhI]^q[Cl^-]^r...$$

$v_{1/2}$ is predicted[28] to be proportional to $k[Pd^{II}]^{(p-1)}[PhI]^q[Cl^-]^r...$, where $[Pd^{II}]$ is the initial concentration of $Pd^{II}X_2(PPh_3)_2$.

and $Pd^0(PPh_3)_4$, 2 mM, in the presence of n-Bu_4NCl, 200 mM, a plot of $1/i_{Ox}^{lim}$ vs time was linear, showing that the rate law is first order in $Pd^0(PPh_3)_4$ and in PhI. An apparent rate constant[9] $k_{ap} = 11.5$ M^{-1} s^{-1} at 20 °C was then determined[34] from the slope of the regression line (correlation coefficient 0.999). A series of identical experiments performed at different temperatures allowed us to evaluate the activation parameters, $\Delta H^{\ddagger} = 95$ kJ mol^{-1} and $\Delta S^{\ddagger} = 101$ J mol^{-1} K^{-1},[35] of the reaction in the presence of n-Bu_4NCl, 200 mM (compare Figure 6a). These results are evidence that chloride ions affect the kinetics of oxidative addition both on enthalpic and entropic grounds.

However, these factors not only characterize the true step of oxidative addition, but also incorporate thermodynamic contributions due to the fast coordination equilibria involving PPh_3 as well as chloride ions (vide infra).[36] Oppositely, the Hammett plot in Figure 6b only characterizes the true step of oxidative addition. Therefore, the difference of Hammett's slopes, i.e., $\rho = 2.7$ in the presence of chloride ions vs $\rho = 2.0$ in absence of chloride ions, shows that the zerovalent palladium center undergoing oxidative addition in the presence of chloride ions strongly differs from that, $Pd^0(PPh_3)_2$, involved in the absence of chloride ions (eq 7). Moreover, the increase of the Hammett slope suggests that this intermediate is more electron rich than $Pd^0(PPh_3)_2$.

Discussion

Mechanism of Oxidative Addition of PhI to Electrogenerated Zerovalent Palladium Species in the Presence of Chloride or Bromide Ions.

Let us first discuss the experimental observations made in the presence of chloride ions. ^{31}P NMR and electrochemical data showed that two-electron reduction of Pd^{II}-$(PPh_3)_2Cl_2$ affords quantitatively three distinct zerovalent palladium-centered species, whose relative concentrations are functions of the palladium and chloride ion concentrations. Interestingly, for the lowest concentrations (mM) of palladium, and/or in the presence of an excess of chloride ions, the ^{31}P NMR signal at 27.14 ppm is not observed. The signal at 25.22 ppm also disappears upon increasing the chloride ion concentration. Finally, in the presence of PhI and under any of the above conditions, all three signals disappear. Such a behavior is consistent with the involvement of three zerovalent palladium species, with different coordination shells. The simplest way to rationalize the effect of palladium concentration is to consider that the species observed at low field (27.14 ppm) is a dimeric species, whereas those observed at intermediate (25.22 ppm) and upperfield (23.15 ppm) are mononuclear. On the other hand, to account for the effect of chloride ion concentration on the respective magnitude of the three signals, one is forced to admit that the two mononuclear species are coordinated by chloride ions, the one observed at upper field bearing more chloride ligand(s) than that observed at 25.22 ppm. Therefore, $Pd^0(PPh_3)_2$, electrogenerated in eq 10, actually consists of three species in equilibrium[16,18,37,38] (P = PPh_3; $m \geq 1$; $n \geq 0$)

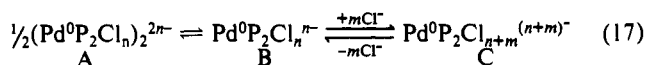(34) (a) Compare $k_{ap} = 16.5$ M^{-1} s^{-1} for the same experiment in the absence of chloride ions. (b) k_{ap} includes a component related to $[PPh_3]$,[9] which under our conditions varies from 1 equiv at $t = 0$ to 2 equiv at completion time. No attempts have been done to correct the data from this perturbation (compare ref 8b).

(35) In the treatment of the Arrhenius plot in Figure 6a, we used a formulation identical with that in ref 8a to allow for an easy comparison of our results to previously published ones obtained in the absence of chloride ions. Thus, $k = (kT/h) \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT)$ was used instead of a more appropriate equation, and $\ln (k/T)$ was plotted instead of $\ln k$.

(36) See ref 8b for a discussion of these aspects.

(37) In eq 7, equilibria are considered (vide infra). However, these equilibria must be slow with respect to NMR so that different peaks are observed for A, B, and C. They must be however rapid within the time scale (>25 μs) of our cyclic voltammetric experiments in order to account for the observation of a single oxidation wave (O).

(38) In eq 17 and in the following, we use an anionic formulation for the zerovalent palladium species ligated by halide ions, instead of a neutral formulation as proposed by Negishi et al.[16] Indeed, under our conditions the only possible countercation is n-Bu_4N^+, which is unlikely to afford bonds or ion pairs with A, B, and C. In particular, observation of these latter species under our conditions demonstrates that their stability is not conditioned by further coordination by a metallic cation, as suggested by the results of Negishi et al.[16]

$$\tfrac{1}{2}(Pd^0P_2Cl_n)_2^{2n-} \rightleftharpoons Pd^0P_2Cl_n^{n-} \underset{-mCl^-}{\overset{+mCl^-}{\rightleftharpoons}} Pd^0P_2Cl_{n+m}^{(n+m)-} \quad (17)$$
$$\text{A} \qquad\qquad \text{B} \qquad\qquad\qquad \text{C}$$

which all react with PhI, either directly, or via displacement of the equilibria in eq 17.

This hypothesis is in qualitative agreement with the electrochemical kinetic observations.[37] Indeed in the absence of added chloride ions, and for the millimolar concentrations of palladium used in cyclic voltammetry, it was found that the oxidative addition of PhI to the electrogenerated zerovalent palladium obeys the rate law in eq 15. Such an apparent trimolecular rate law may be well explained by assuming that the dimeric species A is the most reactive. Indeed, on the basis of the above ^{31}P NMR data, A is not present in solution in the millimolar concentration range considered in transient electrochemistry.[39] Then oxidative addition of PhI to A would continuously displace the equilibria in eq 17 toward the left-hand side

$$2B \rightleftharpoons A \quad (K_{BA}) \qquad\qquad (18)$$

$$A + PhI \rightarrow PhPd^{II}(PPh_3)_2I + \text{etc.} \quad (k_A) \qquad (19)$$
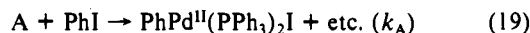
with the result of an overall rate law identical with that in eq 15, with $k = k_A K_{BA}$. On the other hand, according to the ^{31}P NMR data, in the presence of an excess of chloride ions, the equilibria in eq 17 are totally displaced toward its right-hand side. Therefore, if under these conditions the reaction proceeds by oxidative addition to C

$$C + PhI \rightarrow PhPd^{II}(PPh_3)_2I + \text{etc.} \quad (k_C) \qquad (20)$$
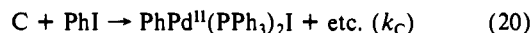
it should appear as being first order in PhI and in zerovalent palladium and zero order in chloride ions. For intermediate values of chloride ion concentrations, none of the equilibria in eq 17 should be totally displaced, which necessarily corresponds to a complex rate law. In agreement with the experimental observations, this rate law is then predicted to be first order in PhI, but with an apparent negative order (between 0 and $-m$) in chloride ions, and an apparent fractional order (between 1 and 2) in palladium.

In the following, we show that these qualitative interpretations can be further substantiated by a quantitative treatment of the electrochemical kinetic results. Considering that the equilibria in eq 17 are fast[37] by comparison to the oxidative addition steps, the rate law for disappearance of zerovalent palladium (i.e., of $[Pd^0] = 2[A] + [B] + [C]$) is as in eq 21:[40]

$$d[Pd^0]/dt =$$
$$-\left(\frac{k_B + k_C K_{BC}[Cl^-]^m + k_A K_{BA}[Pd^0]/(1 + K_{BC}[Cl^-]^m)}{1 + K_{BC}[Cl^-]^m} \right) \times$$
$$[Pd^0][PhI] \qquad (21)$$

where k_A, k_B, and k_C are the rate constants of oxidative addition of PhI to A, B, and C, respectively; $K_{BA} = \{[A]/[B]^2\}_{eq}$ and $K_{BC} = \{[C]/([B][Cl^-]^m)\}_{eq}$ are the equilibrium constants of the two steps in eq 17. The electrochemical data represented in Figures 5a,b were then compared to the predictions based on eq 21. The best fits (compare the solid lines in Figure 5a) were obtained for $m = 1$, which shows that species B and C only differ by the coordination of one chloride ion. Using $m = 1$ allowed the determination of the following kinetic and thermodynamic parameters: $K_{BC} = 70 \pm 10$ M^{-1}, $k_C = 72 \pm 3$ M^{-1} s^{-1}, and $k_A K_{BA} = (9 \pm 2) \times 10^5$ M^{-2} s^{-1}.[41] The value of k_B could not be determined;

(39) On the basis of eq 17 and assuming identical relaxation times for the ^{31}P nuclei in the three species A, B, and C, one may evaluate the equilibrium constant of the dimerization equilibria, $K_{BA} = \{[A]/[B]^2\}_{equil}$, to be in the range of ca. $K_{BA} = 90$ M^{-1}. This corresponds to a ratio ($[A]/[B]$) less than 0.1 under millimolar conditions.

(40) Equation 21 is derived considering also that $2[A] \ll ([B] + [C])$, since for the millimolar solutions considered in cyclic voltammetry, the ^{31}P NMR study predicts that the dimeric species A is not present in the medium at significant concentrations.[39] However, it may participate in the reaction via the process in eqs 18 and 19.

(41) On the basis of the above estimated value of 90 M^{-1} for K_{BA},[39] $k_A \approx 10^4$ M^{-1} s^{-1} can be deduced from the measurement of $k_A K_{BA}$. Compare to $k_C = 72$ M^{-1} s^{-1}.

Role and Effects of Halide Ions on Oxidative Addition

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yet, this does not mean that this step is intrinsically slow.

The data obtained from $Pd^{II}(PPh_3)_2Br_2$ in the presence of bromide ions were interpreted within a similar kinetic framework. Owing to the independence of the data on the initial palladium concentration, it is inferred that, in the presence of bromide ions, the kinetic role of the dimeric species A is negligible, if any, i.e., that $(k_A K_{BA})_{X=Br} \approx 0$. Thus, a simplified version of eq 21 was used to fit the data:

$$d[Pd^0]/dt = -\{k_C + (k_B - k_C)/(1 + K_{BC}[Br^-]^m)\}[Pd^0][PhI] \tag{22}$$

The data in Figure 5c are best represented considering again that $m = 1$, from where it follows that $K_{BC} = 90 \pm 5$ M^{-1}, $k_B = (5 \pm 1) \times 10^2$ M^{-1} s^{-1}, and $k_C = 50 \pm 5$ M^{-1} s^{-1}.

Comparing these values to those obtained in the presence of chloride ions allows us to be more precise about the structures of the palladium-centered species considered in eq 17. Indeed since the relative reactivities of A and B are extremely dependent on the nature of the halide, one is forced to conclude that $n \geq 1$, i.e., that A and B contain at least one halide ligand per palladium center. On the other hand, from the kinetic treatment of the data in Figure 5, we know that $m = 1$, and thus that $n + m = 1 + n \geq 2$. On the basis of general chemical expectations (viz., $n = 1$, $n + m = 2$),[42] the following hypothetical structures for A, B, and C appear to be the most reasonable (X = Cl or Br):[38,43]

(23)
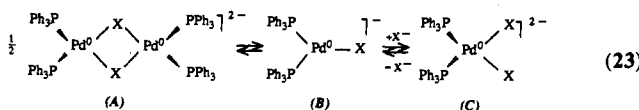
On the basis of these structures, one may find puzzling that, for X = Cl, the fully coordinated species A is more reactive than the unsaturated zerovalent palladium B.[41] Yet, A may be viewed as a "reservoir", prone to release a low-ligated zerovalent palladium moiety $Pd^0(PPh_3)_2$:[13d] For X = Br, A is not involved in the

(24)
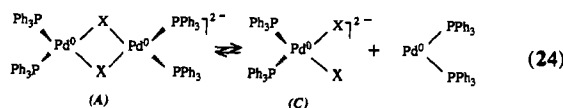
mechanism of oxidative addition of PhI, showing that $(k_A K_{BA})_{Br} \ll (k_A K_{BA})_{Cl}$. This may be related to thermodynamic (viz., $(K_{BA})_{Br} \ll (K_{BA})_{Cl}$, i.e., lesser stability of A vs B, for X = Br than for X = Cl) or kinetic (viz., $(k_A)_{Br} \ll (k_A)_{Cl}$, i.e., lesser reactivity of A vs PhI, for X = Br than for X = Cl) reasons. The thermodynamic hypothesis implies that a bromide ligand has a lesser bridging ability than a chloride vis-a-vis zerovalent palladium centers. The kinetic hypothesis leads to the opposite conclusion, since it implies that eq 24 is more endergonic for X = Br than for X = Cl. This dichotomy cannot be solved on kinetic grounds only. However, we favor the thermodynamic hypothesis. Indeed, on the one hand, the ^{31}P NMR spectrum of a solution of Pd^{II}-$(PPh_3)_2Br_2$, 16 mM, electrolyzed in the absence of added bromide ions shows only the two signals (at 22.30 and 24.49 ppm), whereas that of a solution of $Pd^{II}(PPh_3)_2Cl_2$, 16 mM, electrolyzed under the same conditions exhibits three signals (at 23.15, 25.22, and 27.14 ppm). On the other hand, we know also, from the above kinetic study, that, for X = Br, species B and C are stable under these conditions. This supports the attribution of the two signals at 22.30 and 24.49 ppm to C and B, respectively, and shows that the dimeric species A is not thermodynamically stable under these conditions for X = Br,[44] whereas it has some stability for X =

Cl. This cannot be ascribed to the intrinsic affinity of bromide ion (vs that of chloride ion) for zerovalent centers, since K_{BC} was found to be in the same range for a bromide (ca. 90 M^{-1}) or a chloride (ca. 70 M^{-1}) ligand. This difference is then necessarily related to a difference between the bridging abilities of chloride and bromide ligands in a dinuclear zerovalent palladium complex, by distinction to their similar abilities to coordinate mononuclear zerovalent palladium centers.

Oxidative Addition of PhI to $Pd^0(PPh_3)_4$ in the Presence of an Excess of Chloride Ions. From the ^{31}P NMR data obtained for $Pd^0(PPh_3)_4$ in the presence of an excess of chloride ions, it is deduced that $Pd^0(PPh_3)_3$ is no longer the major palladium-containing species in solution, since its signal at 13.41 ppm is replaced by a signal at 9.68 ppm. Noteworthy, the latter is different from those (23.15, 25.22, and 27.14 ppm) ascribed to A, B, or C in eq 23. We know also that the species observed at 9.68 ppm reacts with PhI at a considerably slower rate than these intermediates, which suggests that it is more strongly coordinated than A, B, or C. The increase by 88 J mol^{-1} K^{-1} of the activation entropy (from 13 J mol^{-1} K^{-1} in the absence of chloride ions to 101 J mol^{-1} K^{-1} in the presence of 200 mM n-Bu_4NCl) of the overall oxidative addition of PhI supports also the hypothesis that this species is more coordinated than $Pd^0(PPh_3)_3$.[45,46] A reasonable structure for this species, meeting all above requirements, is then Pd^0-$(PPh_3)_3Cl^-$.[45b,47]

In the presence of an excess of chloride ions, a Hammett correlation is observed for the oxidative addition of PhI to this species, yet with a slope of 2.7 instead of 2.0 as determined for the same reaction in the absence of chloride ions. This is clear evidence that, in the presence of chloride ions, the transient intermediate involved in the oxidative addition step is different from that reacting with PhI in the absence of chloride ions, being more electron rich. Indeed, if the two intermediates were identical, the apparent overall rate constants k_{ap} should differ, due to the participation of different coordination equilibria, but would necessarily be as in eq 25:[48]

$$d[Pd^0]/dt = -k_{ap}[Pd^0][PhI] \tag{25a}$$

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(42) A larger value for n would imply a coordination number exceeding 4 for palladium centers in species A or C.

(43) In eqs 23 and 24, we favored a tetrahedral coordination for species A and C, and a trigonal coordination for species B, following a suggestion by Dr. O. Eisenstein.

(44) Applying the same method as in footnote 39 to the case of bromide ions, one obtains $(K_{BA})_{Br} \leq 5$ M^{-1}, since no signal is observed for species A in ^{31}P NMR (i.e., its integrated peak is less than 0.05, relative to those observed for B and C). Under millimolar conditions, this would correspond to A amounting to less than 0.5% of the electrogenerated zerovalent palladium.
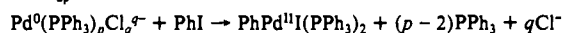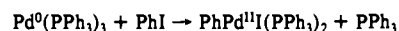
(45) (a) Considering that the structure of Pd^0 in the presence of an excess of chloride ions is $Pd^0(PPh_3)_pCl_q^{r-}$ or aggregates thereof,[16] the overall rate constant k_{ap} relates to the overall reaction

$$Pd^0(PPh_3)_pCl_q^{r-} + PhI \rightarrow PhPd^{II}I(PPh_3)_2 + (p-2)PPh_3 + qCl^-$$

whereas, in the absence of chloride ions it relates to the reaction

$$Pd^0(PPh_3)_3 + PhI \rightarrow PhPd^{II}I(PPh_3)_2 + PPh_3$$

The positive increase of ca. 90 J mol^{-1} K^{-1} of the overall activation entropy then indicates that the sum $p + q$ is larger than 3. (b) Moreover, since rupture of one bond is associated with an average entropy of ca. 85–150 J mol^{-1} K^{-1},[46] it appears reasonable that the rupture of one more bond is involved by comparison to the case of $Pd^0(PPh_3)_3$, i.e., that $p + q = 4$.

(46) Compare to an average activation entropy of ca. -150 J mol^{-1} K^{-1} for S_N2 reactions in organic chemistry. See e.g.: Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; Verlagsgesellschaft: Weinheim, FRG, 1988; p 141.

(47) Considering that the species is $Pd^0(PPh_3)_pCl_q^{r-}$, with $p + q = 4$,[45] implies that $p = 3$ and $q = 1$. Indeed we know that $p = 4$ cannot be retained, since the species would be $Pd^0(PPh_3)_4$, which is not stable under our conditions, even in the absence of Cl^-. Similarly $p = 2$ cannot be considered since the species would be identical with species C, which is in disagreement with the NMR data. Smaller values of p seem difficult to conciliate with the fact that zerovalent palladium electrogenerated in the absence of phosphine has two chloride ligands at most; thus, $q \leq 2$. It follows then that $p = 3$ and $q = 1$, i.e., that the most reasonable structure meeting all the experimental observations is $Pd^0(PPh_3)_3Cl^-$.

(48) The formulation in eqs 25a and 25b assumes that there is only one intermediate reacting with PhI (compare the formulation in eq 21 for the simultaneous reaction several intermediates). This assumption is supported by (a) the fact that in ^{31}P NMR only one species is observed and (b) the fact that a linear correlation is observed in Figure 6b. Indeed, if several transient intermediates compete for p-ZPhI, and the degree of competition changes as a function of the para substituent Z, a curved Hammett plot should be observed, because the intrinsic Hammett correlation for each transient intermediate should differ. Since no trend to curvature is observed, it is concluded that either a single transient intermediate is operative or that the differences among the different intermediates are almost nil so that their intrinsic Hammett slopes are almost identical in order for the degree of competition to be independent of Z. In both situations, the formulation in eqs 25a and 25b remains valid.
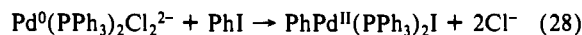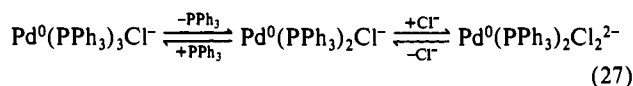
with

$$k_{ap} = \{k_0 / ([PPh_3], [Cl^-])\} \qquad (25b)$$

where k_0 is the intrinsic rate of oxidative addition of PhI to the considered intermediate, whereas $f([PPh_3], [Cl^-])$ is a function of the coordination equilibria leading to the formation of this intermediate and is independent of the aryl halide (compare eq 5' in footnote 9). When the aryl iodide is varied, the variations of $\log (k_{ap}/k_{ap}^H) = \log (k_0/k_0^H)$ should then reflect those of k_0 only, leading to identical slopes for the Hammett correlations under the two conditions. Therefore, the difference of the slopes observed in the presence and in the absence of chloride ions demonstrates that the intermediates reacting with the aryl halide in each case have different k_0 and hence are different. As the reaction remains first order in palladium in both cases, these intermediates may only differ in the number of phosphine and chloride ligands. It is established that, in the absence of chloride ions, the reactive zerovalent palladium is the low-ligated complex $Pd^0(PPh_3)_2$.[8a,b] In the overall reaction of $Pd^0(PPh_3)_3Cl^-$ with PhI, this rules out any mechanism involving a predissociation of the chloride ligand. Indeed, this would generate $Pd^0(PPh_3)_3$, which reacts with PhI via the intermediacy of $Pd^0(PPh_3)_2$. Therefore, one must consider that $Pd^0(PPh_3)_3Cl^-$ reacts with PhI either directly

$$Pd^0(PPh_3)_3Cl^- + PhI \rightarrow PhPd^{II}(PPh_3)_2I + PPh_3 + Cl^- \quad (26)$$
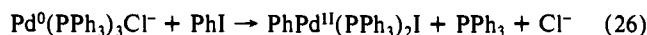
or via the intermediacy of $Pd^0(PPh_3)_2Cl^-$ and $Pd^0(PPh_3)_2Cl_2^{2-}$, formed upon phosphine dissociation and coordination of chloride ions:[49]

$$Pd^0(PPh_3)_3Cl^- \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} Pd^0(PPh_3)_2Cl^- \underset{-Cl^-}{\overset{+Cl^-}{\rightleftharpoons}} Pd^0(PPh_3)_2Cl_2^{2-}$$

$$(27)$$

$$Pd^0(PPh_3)_2Cl_2^{2-} + PhI \rightarrow PhPd^{II}(PPh_3)_2I + 2Cl^- \quad (28)$$

Although it is impossible to conclude which of these two possibilities is correct on the basis of our data only, a direct reaction (eq 26) appears unlikely since $Pd^0(PPh_3)_3$, a less coordinated species than $Pd^0(PPh_3)_3Cl^-$, must proceed via a phosphine dissociation before reacting with PhI (eqs 6 and 7). Conversely, the mechanism in eqs 27 and 28 involves the intermediacy of Pd^0-$(PPh_3)_2Cl^-$ and $Pd^0(PPh_3)_2Cl_2^{2-}$, i.e., of species B and C,[49] which have been identified above as being stable intermediates in the absence of PhI. We are thus enclined to favor this second mechanism (eqs 27 and 28) for the oxidative addition of PhI to $Pd^0(PPh_3)_4$ in the presence of a large excess of chloride ions.

Summary and Conclusions

Generating low-ligated zerovalent complexes by homogeneous or electrochemical reduction of their divalent precursors results in an increase of the overall rate of oxidative addition, by comparison to the reaction of the organic halide with a coordinatively saturated zerovalent metal. This occurs because the method allows one to bypass rather endergonic ligand dissociations from the saturated metal center, with the net result of a considerable increase of the concentration of the active low-ligated form(s) of the zerovalent metal. However, the net gain is not as high as expected on the basis of such simple considerations, because the halide ions generated during the reductive process are not inert but coordinate the low-ligated zerovalent metal. Thus, $Pd^0(PPh_3)_2$, generated by electrochemical reduction of $Pd^{II}(PPh_3)_2Cl_2$, is actually a mixture of three active forms in rapid equilibrium: $[Pd^0(PPh_3)_2Cl]_2^{2-}$ (A), $Pd^0(PPh_3)_2Cl^-$ (B), and $Pd^0(PPh_3)_2Cl_2^{2-}$ (C) (compare Table II). For millimolar concentrations of palladium, the dimeric species A is present only at trace levels in the solution; yet the oxidative addition of PhI proceeds mainly

Table II. Equilibrium Constants and Rate Constants of Oxidative Addition of PhI to $Pd^0(PPh_3)_2$ Electrogenerated from $Pd^{II}X_2(PPh_3)_2$ (X = Cl, Br)[a]

X		$[Pd^0X(PPh_3)_2]_2^{2-}$ (A)	$Pd^0X(PPh_3)_2^-$ (B)	$Pd^0X_2(PPh_3)_2^{2-}$ (C)
Cl	equilibrium constants (M^{-1})	$K_{BA} \approx 90^b$		$K_{BC} = 70 \pm 10$
	rate constants $(M^{-1} s^{-1})$	$k_A \approx 10^{4\,c}$	d	$k_C = 72 \pm 3$
Br	equilibrium constants (M^{-1})	$K_{BA} \leq 5^b$		$K_{BC} = 90 \pm 5$
	rate constants $(M^{-1} s^{-1})$	d	$k_B = 500 \pm 10$	$k_C = 50 \pm 5$

[a] Determined by cyclic voltammetry in THF/0.3 M n-Bu$_4$NBF$_4$, at 20 °C. [b] Estimated from peak integration in ^{31}P NMR, without correction for possibly different relaxation times. [c] Estimated from $k_A K_{BA}$, as determined by cyclic voltammetry, and K_{BA} as estimated from ^{31}P NMR data.[b] [d] Not measurable under our experimental conditions.

through its transient intermediacy, except in the presence of a large excess of chloride ions ($[Cl^-] \geq 0.1$ M). In this latter situation, $Pd^0(PPh_3)_2Cl_2^{2-}$, which is the major species present in the medium, plays the major kinetic role. When $Pd^0(PPh_3)_2$ is electrogenerated by reduction of its dibromide divalent precursor, only two species are involved: $Pd^0(PPh_3)_2Br^-$ and $Pd^0(PPh_3)_2Br_2^{2-}$ (Table II). This seems to point out that bromide ligands have a lower bridging ability for zerovalent palladium centers than chloride ligands.

On purely kinetic grounds, the net effect of the halide coordination is to decrease the overall reactivity of the zerovalent low-ligated species. For example, for a 2 mM solution of Pd^0-$(PPh_3)_2$, an increase from 4 to 200 mM of the chloride ion concentration approximatively results in a 10-fold increase of the half-reaction time with PhI. Yet the longest half-reaction times measured in this study are in the range of 1 s for [PhI] = 10 mM, and are therefore smaller than those determined for $Pd^0(PPh_3)_4$.[8a,b] The stabilization by halide ions should not then be perceived as being detrimental, but rather beneficial from a preparative point of view. Indeed the partial or total saturation of the coordination shell of a zerovalent palladium catalyst by halide ions should prevent its deactivation, e.g., by oligomerization. This may be compared to the empirical finding that, in preparative procedures based on the Heck reaction, the addition of tetraalkylammonium halides to the reaction medium generally greatly improves the yields when the divalent palladium precursor (viz., $Pd^{II}(OAc)_2$, $Pd^{II}(CH_3CN)_2Cl_2$, ...) bears only poorly donating ligands.[20,21]

Although electrochemical methods were essential in unraveling these kinetic and thermodynamic aspects, the above results are not restricted to electrochemical conditions, as shown by the effect of chloride ions on the rate and mechanism of oxidative addition of PhI to $Pd^0(PPh_3)_4$. However, they do not immediately transpose to cases where the low-ligated zerovalent metal is obtained by homogeneous reduction of a divalent precursor by a reducing organometal, R-Met. Then, the cationic center, Met$^+$, formed in the reduction, may participate in the reaction. Indeed, on the one hand, it may decrease the available concentration of free halide ions through specific coordinative properties or through ion pairing. On the other hand, for identical reasons, it may also coordinate the negatively charged zerovalent palladium species[16,18] with the result of enhancing their reactivities. Yet these variations should not result in dramatic kinetic effects since, for example, the half-life of zerovalent palladium electrogenerated by reduction of Pd^{II}-$(PPh_3)_2Cl_2$, 2 mM, in the presence of 1 equiv of PhI and 50 equiv of LiClO$_4$ is only 2 times less than in the absence of LiClO$_4$.

Experimental Section

Chemicals. THF (Janssen) was stored over potassium hydroxide for 24 h and distilled from a sodium benzophenone solution under an argon atmosphere just before use. It was transferred to the cells according to standard Schlenk procedures. n-Bu$_4$NBF$_4$ was obtained from the hydrogen sulfate salt (Janssen), by treatment with NaBF$_4$ (Janssen) in water. It was further recrystallized from ethyl acetate/petroleum ether, dried under vacuum, and stored under argon before use. n-Bu$_4$NCl and n-Bu$_4$NBr were commercial (Janssen). n-Bu$_4$NCl was further recrys-

(49) Under the experimental conditions considered here (i.e., in the presence of 200 mM n-Bu$_4$NCl), the fast phosphine loss in eq 27, giving species B, must be followed by a second fast equilibrium involving the coordination of a second chloride ion to afford species C. Indeed, from the above study of the respective thermodynamic stabilities ($K_{BC} = 70 \pm 10$ M^{-1}) and kinetics of species B and C, the involvement of species C is favored for [Cl$^-$] ≥ 0.1 M (compare Figure 5a).

tallized from acetone/ethyl ether. Both salts were melted and dried under vacuum, and stored under vacuum before use. LiClO₄ (Fluka) was dried under vacuum overnight prior to use. PhI and substituted iodobenzenes were commercial reagents (Janssen) and were distilled or recrystallized before use.

Bis(triphenylphosphine)palladium dichloride was synthesized from Na₂PdCl₄ and PPh₃ according to a published procedure.[50] Bis(triphenylphosphine)palladium dibromide or diiodide was synthesized by the same procedure but in the presence of 100 equiv of KBr or KI, respectively.[50]

Tetrakis(triphenylphosphine)palladium was synthesized, according to a published procedure, by reduction of Pd^{II}Cl₂(PPh₃)₂ by NaBH₄ in the presence of 2.5 equiv of PPh₃.[50,51]

trans-PhPd(PPh₃)₂I was synthesized according to Fitton's procedure.[52] ¹H NMR (250 MHz in CDCl₃ vs TMS): 6.25 ppm (t $J = 7.5$ Hz, 2 H); 6.36 (t $J = 7.5$ Hz, 1 H); 6.63 (d $J = 7.5$ Hz, 2 H); 7.3 (m, 18 H); 7.54 (m, 12 H).

³¹P NMR spectrometry was performed in THF on a Bruker spectrometer (162 MHz) using H₃PO₄ as the internal reference. ¹H NMR spectrometry was performed in CDCl₃ on a Bruker AC-250 MHz using TMS as the internal reference.

Electrochemical Setup and Electrochemical Procedure for Cyclic Voltammetry of Double Potential Step Chronoamperometry. Cyclic voltammetry and double potential step chronoamperometry were performed as described in previous works of this group.[5,27d] A home-built potentiostat equipped with positive feedback for ohmic-drop compensation was used.[53] The reference electrode was a SCE (Tacussel) separated from the solution by a bridge (3 mL) filled with a *n*-Bu₄NBF₄ solution in THF identical with that used in the cell. All potentials given here refer to this reference electrode. All the experiments reported here were performed at 20 °C, except for those related to determination of activation parameters.

Electron consumptions in transient electrochemistry were determined following a method recently described that combines the use of classical working electrodes and ultramicroelectrodes (20 or 10 μm diameter gold disks).[23]

General Procedure for Preparative Scale Electrochemistry. A 40-mL portion of THF and 2.7 g of *n*-Bu₄NBF₄ were introduced into each compartment of the cell under argon atmosphere. For example, 0.45 g (0.64 mmol, 16 mM) of Pd^{II}Cl₂(PPh₃)₂ and the required amount of *n*-Bu₄NCl were introduced into the cathodic compartment. Electrolysis was then performed by setting the potential on the plateau of wave R (or of R₂ whenever wave R split into waves R₁ and R₂) and was interrupted after the current dropped to ca. 5% of its initial value. Charge integration showed that this limit corresponded within a few percent to 2 faradays/mol of Pd^{II}Cl₂(PPh₃)₂. For ³¹P NMR studies, an NMR tube filled with argon and equipped with a septum was filled with this solution by using a cannula according to standard Schlenk procedures. After recording of the ³¹P NMR spectra, 10 equiv of degassed PhI was introduced into the NMR tube through the septum cap, and a new set of ³¹P NMR spectra were recorded to ensure that the final product of the reaction was *trans*-PhPd^{II}(PPh₃)₂, by comparison to the spectra of an authentic sample under the same conditions.

General Procedure for Kinetics of Oxidative Addition of Substituted Iodobenzenes to Pd⁰(PPH₃)₄. The cell was connected to a Schlenk line, and three vacuum–argon cycles were performed. A 12-mL portion of THF/0.3 M *n*-Bu₄NBF₄ (1.2 g) was then introduced into the cell (3 mL of the same solution was introduced into the bridge compartment of the reference electrode) according to Schlenk techniques. A 27.7-mg (0.024 mmol, 2 mM) portion of Pd⁰(PPh₃)₄ was then added to the cell, together with the selected amount of *n*-Bu₄NCl. After the cell was thermostated at the selected temperature, the RDE was polarized on the plateau of the oxidation wave of Pd⁰(PPh₃)₄, and the oxidation current was monitored

as a function of time to ensure that no passivation of the electrode occurred. At time zero a stoichiometric amount of substituted iodobenzene was added to the cell and the current recorded up to 95% conversion. The current data were then treated as described in the text.

Effect of LiClO₄ on the Reactivity of Zerovalent Palladium Electrogenerated by Reduction of Pd^{II}(PPh₃)₂Cl₂. Cyclic voltammograms of 2 mM Pd^{II}(PPh₃)₂Cl₂ in the presence of 2 mM PhI were performed in THF/0.3 M *n*-Bu₄NBF₄, in the absence or in the presence of 100 mM LiClO₄. The respective sizes of waves R and O (see, e.g., Figure 1) on a voltammogram obtained in the presence of LiClO4, at a scan rate v, were identical with those observed on a voltammogram obtained at a scan rate $v/2$ in the absence of LiClO₄. This established[28,33] that the reactivity of zerovalent palladium electrogenerated by reduction of Pd^{II}(PPh₃)₂Cl₂ in the presence of LiClO₄ (50 equiv) is twice that observed in the absence of LiClO₄.

Relationships between $v_{1/2}$ and Rate Constants. The theoretical relationships corresponding to the various rate laws presented in this work have been determined by numerical simulation of each individual voltammogram or chronoamperogram. For cases corresponding to a single rate-determining step, the simulated voltammograms were obtained according to classical procedures in use in electrochemical kinetics.[25,56] It was then established that, for the conditions used in this study, the following relationships between $v_{1/2}$ and the overall pseudo rate constant $v_{1/2} = 2.227k$ (respectively $v_{1/2} = 0.7980kC^0$, C^0 being the initial concentration of divalent palladium complex) could be used for a pseudo-first-order (respectively a pseudo-second-order) process. These relationships were tested by independent simulation[56] and shown to afford $v_{1/2}$ values within a few percent accuracy, i.e., considerably better than that of experimental determinations of $v_{1/2}$.

For cases where two or more reactions compete for the kinetic control of the voltammogram, a simplified procedure was devised owing to the overwhelming number of simulations that would have been required for the fitting of the data in Figure 5, according to classical electrochemical procedures. This simplified procedure consisted in assuming that $v_{1/2}$ for the rate law in eq 21, viz.

$$d[Pd^0]/dt = -k_1[Pd^0] - k_2[Pd^0]^2$$

with

$$k_1 = \{(k_B + k_C K_{BC}[X^-]^m)/(1 + K_{BC}[X^-]^m)\}[PhI]$$

and

$$k_2 = \{k_A K_{BA}/(1 + K_{BC}[X^-]^m)^2\}[PhI]$$

was the sum $(v_{1/2})_1 + (v_{1/2})_2$ of the two independent $v_{1/2}$ values that were obtained by considering that $k_2 = 0$ or $k_1 = 0$, respectively. Owing to the above relationships between $(v_{1/2})_1$ and k_1 or between $(v_{1/2})_2$ and k_2C^0, it ensued that $v_{1/2} = 2.227k_1 + 0.7980k_2C^0$, i.e., considering the above values of k_1 and k_2

$$v_{1/2} = \left(\frac{2.227(k_B + k_C K_{BC}[X^-]^m) + 0.7980 k_A K_{BA} C^0/(1 + K_{BC}[X^-]^m)}{(1 + K_{BC}[X^-]^m)} \right) \times [PhI]$$

This analytical approximated expression was used in the fitting procedures of the data in Figure 5. The validity of this procedure was checked by independent test simulations[56] and shown to introduce an error less than 10% on $v_{1/2}$. Such an error would correspond to an uncertainty less than 1.35% on the current peak of wave O, and is therefore much less than experimental uncertainty (ca. 5%) on this variable.

In the above equation, $[X^-] = [n\text{-}Bu_4NX] + 1.5[Pd^{II}(PPh_3)_2X_2]$ was used to account for the partial release of halide ions upon electrolysis. Via an iteration procedure, more precise values of $[X^-]$ could then be evaluated. Yet the above approximate expression was shown to introduce an error less than 5% for the points on the left-hand side of Figure 5a, and a negligible error for the other data in Figure 5.

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(54) (a) In cyclic voltammetry, two time scales are involved in experiments such as those described. A first time scale, $\theta_1 = (RT/ anFv)$,[25] governs the peak shapes and peak locations. A second time scale, here $\theta_2 \approx (E^P_R - 2E_{inv} + E^P_O)/v$ or $(E^P_{R2} - 2E_{inv} + E^P_O)/v$,[55] governs the chemical stability of the zerovalent palladium species electrogenerated at wave R (or at wave R₂, accordingly), and therefore controls only the magnitude of wave O. (b) For determination of the proper pulse potentials values, one has thus to consider that $\theta = \theta_1$, whereas $R(\theta)$ in eq 13 corresponds with $r(v)$ in eq 14, when $\theta = \theta_2$.
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(56) Simulations of cyclic voltammograms were performed by using the *General Program of Simulation* provided to us by its author, Dr. David K. Gosser Jr.

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Observations of Nonadditive Substituent Effects on the Dimethyl Sulfoxide Solution Homolytic Bond Strengths of Anthrylmethyl C–H Bonds

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Abstract: Acid–base and redox data, when incorporated into a thermochemical cycle, enable accurate determination of the effects of substituents on the homolytic strengths of chemical bonds. In this study, the effects of substituents on the dimethyl sulfoxide phase homolytic strengths of labile sp^3 C–H bonds present in 9-methylanthracene, seven variously substituted 9-methylanthracenes, phenylacetonitrile, and α-methoxyphenylacetonitrile are evaluated. The bond-strength data for these species indicate that, when present individually, 10-cyano and α-methoxy substituents weaken the anthrylmethyl C–H bond in 9-methylanthracene (in a homolytic sense) by 1–2 and 4 kcal/mol, respectively. When both 10-cyano and α-methoxy substituents are present in the same molecule, as in 10-cyano-9-(methoxymethyl)anthracene, the anthrylmethyl sp^3 C–H bond is weakened by 8 kcal/mol. Therefore, the bond-weakening effect of a 10-cyano substituent on 9-methylanthracene sp^3 C–H bond strengths is ca. 2 kcal/mol greater when the C–H bond to be cleaved is adjacent to an α-methoxy substituent. A similar and somewhat larger synergism (ca. 4 kcal/mol) is observed when an α-phenoxy substituent is present in place of α-methoxy. In related experiments, an α-cyano substituent is shown to weaken the anthrylmethyl C–H bond in 9-methylanthracene by ca. 3 kcal/mol. These data constitute the first nonkinetic experimental observations of synergistic substituent effects on the homolytic strengths of sp^3 C–H bonds. While not necessarily indicative of a general phenomenon, the observed changes in 9-methylanthracene sp^3 C–H homolytic bond strengths (due to the simultaneous presence of α-methoxy (or α-phenoxy) and 10-cyano substituents) can be rationalized by invoking a solvent-induced stabilization in the incipient anthrylmethyl radicals that results from the presence of both donor and acceptor substituents in conjugation with the unpaired electron.

The fact that Hammett ρ values for plots of pK_a vs Hammett σ for a pair of structurally similar families of acids (e.g., for 4-substituted phenylacetonitriles and 4-substituted phenylmalononitriles dissolved in dimethyl sulfoxide (DMSO) solution) are nonequal (7.0 and 5.5, respectively) requires nonadditive substituent effects on the acid–base equilibria for these species in DMSO solution.[1] Nonadditive substituent effects on the pK_a's for these species are best rationalized by pointing out that the additional α-cyano substituent present in the phenylmalononitrile family acts to reduce the amount of negative charge available for delocalization into the phenyl ring in the conjugate bases derived from the respective phenylmalononitriles relative to the amount of delocalization into the phenyl ring in the conjugate bases derived from the respective phenylacetonitriles. A given electron-accepting substituent, therefore, acidifies phenylmalononitrile to a lesser extent compared to its effect on the acidity of phenylacetonitrile. The pK_a data therefore suggest that interactions between negative charge density and multiple (nonsterically demanding) substituents are not additive and that the nonadditivities affect the stabilization of solution-phase organic anions.

Whereas the effects of multiple substituents on anion stabilities are reasonably well-understood, the effects of multiple substituents on radical stabilities are a source of disagreement and uncertainty. Several investigators have suggested that the simultaneous presence of donor and acceptor groups stabilizes organic radicals greater than would be expected on the basis of the individual contributions of either substituent if present singly.[2-6] The terms "push-pull

resonance",[3] "merostabilization",[4] and "captodative"[5] have been used to describe the synergism that results from the presence of both donor and acceptor substituents. Kinetic data have been used to support[7] as well as deny[8] the existence of nonadditive (i.e., synergistic) substituent effects on radical stabilities. More recently, additional theoretical results have been published that cast doubt on the general existence of any dipolar resonance contribution to radical stabilization,[9] in contrast to an earlier report that suggested synergistic substituent effects will be observed only when the appropriately substituted radical is dissolved in a solvent of high polarity.[10] Other investigators, while noting that the absence of saturation effects on homolytic bond dissociation energies (BDEs) indicates that the presence of powerful donor and acceptor groups

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