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Mechanism of Oxidative Addition of Palladium(0) with Aromatic Iodides in Toluene, Monitored at Ultramicroelectrodes

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The mechanism and rates of oxidative addition of substituted iodobenzenes to tetrakis(triphenylphosphine)palladium(0) is investigated in toluene by means of electrochemistry at ultramicroelectrodes. The mechanism is shown to be identical with that previously reported in THF and to correspond to a similar slope for Hammett's correlation ($\rho = +2$ in THF vs $+2.3 \pm 0.2$ in toluene). Moreover, the important change in polarity ($\epsilon_s \approx 7.58$ in THF and 2.38 in toluene) does not affect the enthalpy of activation and leads to similar activation entropies in both solvents. This suggests that the transition state of addition of aryl halides to the coordinatively unsaturated zerovalent palladium complex $Pd^0(PPh_3)_2$ has no significant ionic character.

Introduction

Oxidative addition is a ubiquitous reaction involved in many synthetic metal-catalyzed processes.[1,2] Indeed, it amounts to the conversion of organic substrates into organometallic intermediates, which may undergo selective and rapid follow-up reactions:

$$RX + M^0 \rightarrow R\text{-}M^{II}\text{-}X \rightarrow \text{etc.} \qquad (1)$$

The products of oxidative addition are generally well characterized, yet their exact mechanism of formation is still debated. Different mechanisms have been proposed,[3-9] involving either concerted two-electron transformations or a succession of elementary steps initiated by a single-electron transfer from the zerovalent metal to the organic substrate.[6,7,9] To simplify the following discussion, they can be viewed as variations[4c] of one of the two limiting mechanisms presented in Scheme I, where route i features concerted reactions involving a neutral transition state and route ii illustrates mechanisms taking place via ionic transition states or intermediates.

The difficulty in distinguishing kinetically between mechanisms belonging to these two limiting classes originates from the fact that they are all subject to the same trends in electronic, and presumably steric, effects. Indeed for both limiting situations in Scheme I, the rate of oxidative addition is predicted to increase with the reducing properties of the metal center as well as with the decrease of the reduction potential of the organic substrate. Therefore, discrimination of the two mechanisms on the basis of correlations between the rate constant of oxidative addition and the driving force for single-electron transfer remains delicate to difficult.[10,11]

The two mechanisms could be distinguished on the basis of their activation entropies. Indeed the concerted path (i) in Scheme I involves a specific organization of the organic and metallic moieties in the activated complex, which should be reflected by a large activation entropy.[13] By comparison an outer-sphere electron transfer should involve a relatively small entropy of activation. However, the experimental determination of activation entropies is hampered by the fact that the oxidative addition in eq 1 involves a transient coordinatively unsaturated form of the zerovalent metal. Indeed, zerovalent metals such as nickel, palladium, etc. are available as their chemically stable tetrasubstituted derivatives, ML_4, whereas the active form in eq 1 is the highly reactive, coordinatively unsaturated moiety ML_2.[14,15] Therefore, the reaction involves a series

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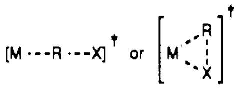
(1) For reviews on oxidative addition see e.g. (a) Collman, J. P. *Acc. Chem. Res.* **1968**, *1*, 136. (b) Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 53. (c) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386. (d) *Transition Metal Organometallics in Organic Synthesis*, Alper, M., Ed.; Academic Press: New York, 1976. (e) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434. (f) Tsuji, J. *Fortsch. Chem. Forsch.* **1972**, *28*, 41.

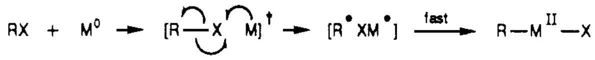
(2) For synthetic applications of oxidative addition of zerovalent palladium complexes, see e.g.: (a) Heck, R. F. *Pure Appl. Chem.* **1978**, *50*, 691. (b) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669. (c) Negishi, E. I. *Acc. Chem. Res.* **1982**, *15*, 340.

(3) For a complete discussion of the various mechanisms proposed for oxidative addition see: Kochi, J. K. In *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Part I, Chapter 7, pp 156-183.

(4) As discussed in ref 3 (see e.g. pp 157 or 176-177), several other mechanisms have been proposed for oxidative addition: (a) For example, the concerted process (i) in Scheme I has been considered to involve either a two- or three-center transition state[5]



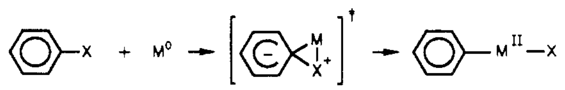
or to proceed via a radical "nonchain"[6]



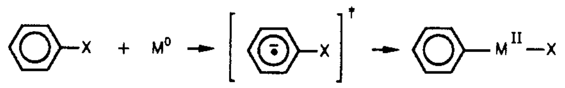
or a radical chain[7]

$$RX + RM^0 \rightarrow R\text{-}M^{II}\text{-}X + R^{\bullet}$$
$$R^{\bullet} + M^0 \rightarrow RM^0, \text{etc.}$$

(b) Transition states possessing an ionic character, as that considered in route ii of Scheme I, have been proposed, e.g.[8]



or[9]



(c) Therefore, the dichotomy presented in Scheme I is to be viewed as a simplistic illustration of "*nonionic*" transition states (route i) as opposed to "*ionic*" transition states (route ii).

(5) For example, $Pd^0(PPh_3)_4$ reacts with $PhCH(CH_3)Br$ with 95% inversion of configuration at carbon (Lau, K. S. Y.; Wong, P. K.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5832), a result that favors a S_N2-like transition state. For a three-center transition state for $Rh(CH_3)(PPh_3)_3$ and PhI, see also: Semmelhack, M. F.; Ryono, L. *Tetrahedron Lett.* **1973**, 2967.

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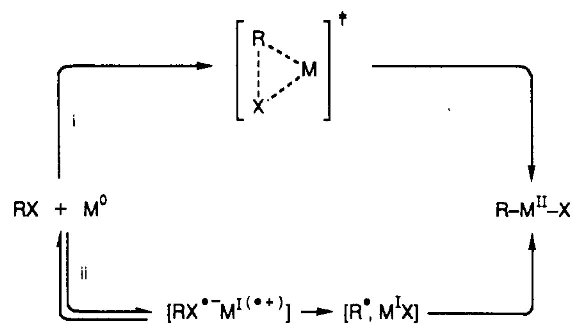
Scheme I



of two fast preequilibria, in eqs 2 and 3, prior to the very act of oxidative addition occurring in eq 4.

$$M^0L_4 \rightleftharpoons M^0L_3 + L \quad K_1 \qquad (2)$$

$$M^0L_3 \rightleftharpoons M^0L_2 + L \quad K_2 \qquad (3)$$

$$M^0L_2 + RX \rightarrow R\text{-}M^{II}L_2\text{-}X \quad k \qquad (4)$$

$$k^{exp} = k/(1 + [L]/K_2 + [L]^2/K_1K_2) \qquad (5)$$

Thus, the experimental rate constant for the overall reaction is formally given as in eq 5. Generally, $K_1 \gg [L]$ under the conditions of kinetic experiments,[16] whereas[17] $K_2 \ll [L]$, as evidenced by experimental rate laws such as that in eq 6[8a,9a] (see also later), where $[M^0]$ represents the overall concentration in zerovalent metal irrespective of its degree of coordination.

$$d[M^0]/dt = -kK_2[M^0][RX]/[L] \qquad (6)$$

As a result, the *experimental* activation parameters $\Delta H^‡(\text{exp}) = \Delta H^‡ + \Delta H_2°$ and $\Delta S^‡(\text{exp}) = \Delta S^‡ + \Delta S_2°$ include unknown thermodynamic contributions, $\Delta H_2°$ and $\Delta S_2°$, which pertain to the fast preequilibrium in eq 3. These preclude the use of activation parameters to discriminate between the two limiting paths in Scheme I, unless K_2 is determined independently.[17] However, K_1 and K_2, being relative to equilibria between neutral species, are considered to be relatively independent of the solvent polarity.[1b,e,f,3,9,18] Therefore, variations, if any, of the experimental activation parameters upon modification of solvent polarity should be mainly indicative of variations in $\Delta H^‡$ and $\Delta S^‡$ and relative to the very act of oxidative addition in eq 4.[9a] Similarly, possible variations of the slope of Hammett's correlations, obtained in solvents of different dielectric constants, should relate only to variations in the activation parameters of eq 4, since K_1 and K_2 are constant within a solvent.

In the following, we want to take advantage of such possible changes in activation parameters upon variation of dielectric constant of the solvent, to distinguish between the two pathways in Scheme I. The concerted pathways, noted as path i in Scheme I, formally involve no creation of charges in its transition state. Therefore, it should be rather insensitive to polar changes of the solvent. Oppositely, the single-electron-transfer and ionic pathways, which correspond to the formation of an ion pair either in its transition state or in the electron-transfer preequilibrium, should be very sensitive to polar changes of the medium.[19]

In order to examine such effects, we decided to investigate the role of solvent polarity in the reaction of $Pd^0(PPh_3)_4$ with a series of substituted iodobenzenes.

Results

The mechanism of oxidative addition of aryl iodides to $Pd^0(PPh_3)_4$, and the corresponding activation parameters, measured in the range 0–50 °C, have been reported in THF.[8a] Owing to the poor definition of the UV–visible absorption of the palladium complex in the reaction medium,[20] the kinetics of the reaction could not be monitored by spectroscopy. However, it was shown[8a] that monitoring of the current plateau of the electrochemical oxidation wave of the tetrakis(triphenylphosphine)palladium(0) complex (uncorrected half-wave potential[21] $E_{1/2} = 0.47$ V vs Ag/Ag$^+$, 0.1 M in THF[8a] was a convenient method for following its concentration changes, since the products of

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(6) See e.g.: (a) Bradley, J. S.; Connor, D. E.; Dolphin, D.; Labinger, J. A.; Osborn, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 4043. (b) Labinger, J. A.; Kramer, A. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 7908.

(7) Such a radical chain was proposed for $Pt(PEt_3)_3$ by: Kramer, A. V.; Labinger, J. A.; Bradley, J. S.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 7145.

(8) Compare e.g.: (a) Fauvarque, J. F.; Pflüger, F.; Troupel, M. *J. Organomet. Chem.* **1981**, *208*, 419. (b) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

(9) For the reaction of Ni^0P_4 (P = phosphine) with electron acceptors, see e.g.: (a) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319. (b) Elson, I. E.; Morrell, D. G.; Kochi, J. K. *J. Organomet. Chem.* **1975**, *84*, C7.

(10) Similarly, use of stereochemical approaches remains delicate because "in-cage" reactions are involved[11] or because ligand exchange at the metal center may result in alteration of the stereochemistry of the primary product of oxidative addition.

(11) Compare to the same problem arising in distinctions between S_N2 and single-electron-transfer (SET) mechanisms in organic chemistry. See e.g.: (a) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. (b) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197. For recognition of SET pathways in organometallic chemistry, see: Kochi, J. K. In ref 3.

(12) Generally at least on the order of −30 to −40 eu (i.e. −130 to −160 J K^{-1} mol^{-1}). Compare e.g.: Reichardt, C. In *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; Verlagsgesellschaft: Weinheim, FRG, 1988; p 141.

(13) (a) Outer-sphere electron transfers are associated with low activation entropies, since they require only small and nonspecific interactions (less than a few kJ mol^{-1}) between the two centers; see e.g.: Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Conversely, inner-sphere electron transfers require higher and specific interactions within the transition state.

(14) (a) See a discussion of this point for $Ni^0(PEt_3)_4$: Reference 9, p 6325. (b) For other zerovalent metals and phosphine ligands, see: Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

(15) (a) For the Ni^0(dppe) reaction with PhBr, see: Amatore, C.; Jutand, A. *Organometallics* **1988**, *7*, 2203. (b) For $Pd^0(PPh_3)_2$, with PhI and PhBr, see: Amatore, C.; Azzabi, M.; Jutand, A. *J. Organomet. Chem.* **1989**, *363*, C41, and relevant work to be submitted for publication.

(16) For $Ni^0(PEt_3)_4$, K_1 is measured to be ca. 10^{-2} M.[14]

(17) (a) For $Ni^0(PEt_3)_4$, K_2 was estimated as being smaller than 10^{-6} M.[14] (b) A similar result is obtained in ref 15a. (c) For $Pd^0(PPh_3)_4$ in THF, $K_2 = 1.5 \times 10^{-5}$ M has been determined in the presence of chloride ions: Amatore, C.; Azzabi, M.; Jutand, A. To be submittted for publication.

(18) See e.g. ref 9, p 6323.

(19) (a) For the effect of solvent polarity on a transition state possessing ionic character in organic chemistry, see e.g.: Reichardt, C. In ref 12, p 140. (b) For a recent discussion of such effects in an analogous situation (viz. "ionic" vs "nonionic" route) see: Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227.

(20) Although they have a slight yellow color, (triphenylphosphine)palladium(0) complexes do not show definite characteristic UV–visible absorptions in THF[8] or toluene, at wavelengths longer than those corresponding to the free or ligated triphenylphosphine.

(21) Control of the potential of an electrode is made with respect to that of the bulk of the solution.[22a] Therefore, the true potential difference is $E + iR$[22b] (where E is the overall applied voltage and i the current flowing through the cell of electrical resistance R). In solvents with relatively large dielectric constants ($\epsilon \geq 30$), and in the presence of decimolar concentrations of an inert electrolyte, R is on the order of a few kiloohms or less, at an electrode of millimetric size. The current being in the range of a few microamperes, the "ohmic drop" term iR is generally on the order of tens of millivolts. The voltammograms are therefore only slightly distorted and bear meaningful kinetic information on the processes going on at the working electrode. In low-dissociating solvents R is greatly increased, with the result that the voltammograms represent generally only ohmic phenomena ($iR \approx E$).

(22) (a) See e.g.: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980. (b) Owing to the usual electrochemical conventions, cathodic potentials are negative, whereas reductive currents are given positively; the converse is respectively true for anodic conditions. Thus, $E + iR$ generally has a lower magnitude than the "imposed" potential E.

the reaction, $ArPdI(PPh_3)_2$ and triphenylphosphine, do not show any electrochemical activity in the same potential range.

The same technique, i.e. amperometry at a rotating-disk electrode (RDE), is applicable in other solvents. Yet it would only allow examination of the reaction in solvents with dielectric constants larger than that of THF ($\epsilon_s = 7.58$) because of experimental difficulties related to the large resistivities of solutions in solvents of lower dielectric constants.[21] On the other hand, most of the suitable electrochemical solvents[23] present nucleophilic properties or possible reactivity with zerovalent transition metals, which preclude their use in this study, since they might interfere in the mechanism of oxidative addition.

The recent development of ultramicroelectrodes,[24] whose sizes are in the range of a few micrometers or less, has allowed significant electrochemical data to be obtained in highly resistive media as, for example, in the absence of supporting electrolyte[25] or in solvents such as toluene and hexane.[26,27] Moreover, steady-state voltammograms, whose plateau currents are independent of convection and remain proportional to the concentration of the electroactive species, are obtained at ultramicroelectrodes, independently of the degree of stirring of the solutions,[29] under usual laboratory conditions. Ultramicroelectrodes provide therefore a unique opportunity for studying the kinetics of oxidative addition in a solvent with dielectric constant lower than that of THF, such as toluene ($\epsilon_s = 2.38$).

Electrochemical Oxidation of Tetrakis(triphenylphosphine)palladium(0) Complexes in Toluene. Although problems related to ohmic drop are considerably reduced at ultramicroelectrodes,[27] one cannot combine the difficulties arising from an extremely low dielectric constant with those related to the absence of supporting electrolyte. Therefore, the electrochemical oxidation of $Pd^0(PPh_3)_4$ was investigated in toluene with 0.06 M $NHex_4BF_4$ as the supporting electrolyte. This concentration was selected as an optimum between reduction of ohmic drop, on the one hand, and solubility and large increase of the viscosity of the solution at higher concentrations, on the other hand. For these solutions, no electrochemical data could be obtained at electrodes of millimetric diameters, although an easily recognizable electrochemical oxidation wave is observed at ultramicroelectrodes for $Pd^0(PPh_3)_4$, at millimolar concentrations, as shown in Figure 1a. Owing to the large electrical resistance of the medium ($R_u \approx 200-300$ MΩ at 20 °C; see Experimental Section and Figure 1c), these voltammograms are distorted by ohmic drop,[21] as evidenced by their small slopes around $E_{1/2}$ and the variations of their half-wave potentials, $E_{1/2}$, with concentration (Figure 1c). Nevertheless, the steady-state voltammograms in Figure 1a present definite plateau currents,[31] whose values are proportional to the Pd(0) concentration. Moreover, these voltammograms can easily be corrected for the ohmic drop contribution by replotting the current, i, as a function of the true electrode potential, $E - iR_u$, as shown in Figure 1b (see Experimental Section). This allows the half-wave potential to be measured as −0.53 V vs $Ag/AgBF_4$ (0.1 M in toluene, 0.06 M $NHex_4BF_4$).

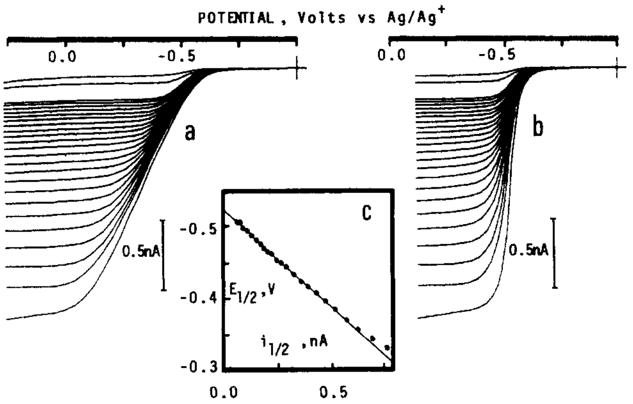

Figure 1. Voltammograms obtained at 25 °C for the oxidation of $Pd^0(PPh_3)_4$ at different concentrations (1.5 mM for the voltammogram with the largest oxidation current in (a) and (b)) in toluene, 0.06 M n-Hex_4NBF_4, in the presence of 50 mM PPh_3 (5-μm-radius gold-disk ultramicroelectrode; scan rate $v = 0.2$ V s^{-1}): (a) uncorrected voltammograms; (b) voltammograms corrected for ohmic drop contributions (see Experimental Section); (c) variations of the half-wave potential, $E_{1/2}$, with $i_{1/2} = i_{lim}/2$, for the voltammograms shown in (a) (the regression line corresponds to $E_{1/2} = -0.53$ V vs Ag/Ag^+ and $R_u = 270$ MΩ). Potentials are referred to the $Ag/AgBF_4$ (0.1 M) reference electrode in toluene, 0.06 M $NHex_4BF_4$.

Provided that the solutions were kept oxygen-free, no degradation was observed over periods of ca. 1 h. However, keeping the electrode potential on the plateau of the Pd^0 wave resulted, after a few minutes, in a slow decrease of the current with time. This phenomenon, which was tentatively ascribed to a progressive blocking of the electrode by adsorption, could be suppressed by regenerating the electrode surface by extending the negative potential scan up to ca. −2.7 V vs 0.1 M Ag/Ag^+, between the

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(23) See: Mann, C. K. In *Electroanalytical Chemistry*; Bard, A. J.; Ed.; Dekker: New York, 1969, Vol. 3, pp 57–134.

(24) For a recent and documented review on ultramicroelectrodes, see: Wightman, R. M.; Wipf, D. O. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1989; Vol. 15, pp 267–353.

(25) For an experimental illustration and theory of voltammetry under conditions of low ionic strength, see e.g.: (a) Amatore, C.; Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *220*, 49. (b) Amatore, C.; Fosset, B.; Bartelt, J.; Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *256*, 255.

(26) For the earliest use of a solvent of low dielectric constant in electrochemistry at ultramicroelectrodes see e.g.: (a) Lines, R.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1977**, *B31*, 369. (b) Howell, J. O.; Wightman, R. M. *J. Phys. Chem.* **1984**, *88*, 3915. (c) Geng, L.; Ewing, A. G.; Jernigan, J. C.; Murray, R. W. *Anal. Chem.* **1986**, *58*, 852. (d) Geng, L.; Murray, R. W. *Inorg. Chem.* **1986**, *25*, 3115.

(27) The unique capabilities of ultramicroelectrodes that allow electrochemistry to be performed in highly resistive media[24–26] stem from the fact that the electrical resistance R of a solution of resistivity ρ at an electrode of radius r_0 is proportional to ρ/r_0. On the other hand, the current under transient conditions[28] is proportional to the electrode surface area, i.e. to r_0^2; the "ohmic drop", iR,[21] is therefore directly proportional to r_0 and goes to zero when the latter is decreased.

(28) Under steady-state conditions, e.g. at a disk electrode such as that used in this study, $i \propto 1/r_0$, and therefore iR tends to be a constant. See e.g.: Bruckenstein, S. *Anal. Chem.* **1987**, *59*, 2098. This constant term is, however, always smaller than that observed under transient conditions[27] at the same electrode.

(29) The steady-state behavior observed at ultramicroelectrodes originates from nonlinear diffusion[24,30] and not from hydrodynamics as, for example, for the rotating-disk electrode (RDE) or polarography.[22a] Therefore, the currents observed are independent of the hydrodynamic properties of solutions found under usual experimental conditions (e.g. magnetic stirring or laboratory mechanical stirring).

(30) (a) Amatore, C. In *Ultramicroelectrodes*; Fleishmann, M., Pons, S., Rolison, D. R., Schmidt, P., Eds.; Datatech Science: Morganton, NC, 1987. For diffusion at disk electrodes, see e.g.: (b) Oldham, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *122*, 1. (c) For other geometries such as band or cylindrical electrodes, see: Amatore, C.; Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *206*, 23. Deakin, M. R.; Wightman, R. M.; Amatore, C. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *215*, 49. Amatore, C.; Fosset, B.; Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *227*, 33.

(31) As soon as a current plateau is observed, its current value is independent of ohmic drop effects.[21] Indeed, the current plateau corresponds to a zero concentration of the electroactive species at the electrode surface,[22a] which then becomes independent of the exact value of the electrode potential. However, the rising portion of the voltammogram, and therefore $E_{1/2}$ values, may be considerably affected; compare e.g. Figure 1.

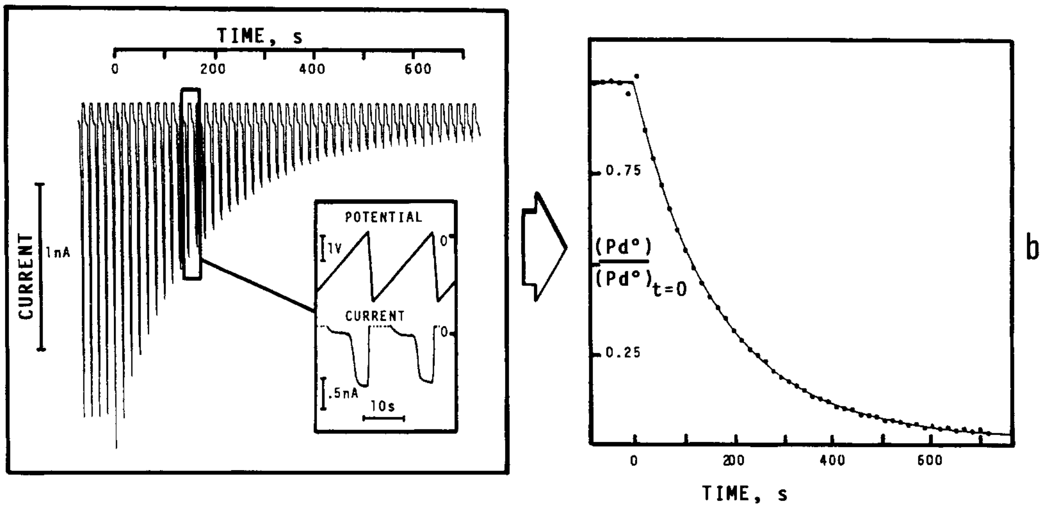

Figure 2. Variation of $Pd^0(PPh_3)_4$ concentration as a function of time, during its reaction with *p*-iodotoluene in toluene, 0.06 M $NHex_4BF_4$, at 25 °C, monitored electrochemically at a 5-μm-radius gold-disk ultramicroelectrode (see Experimental Section and Figure 1): (a) display of the voltammograms as a function of time two successive voltammograms being shown in the insert (the cathodic current portion is deleted for simplification), together with the corresponding potential/time wave function; (b) resulting variation of $Pd^0(PPh_3)_4$ concentration with time (the solid line corresponds to the rate law in eq 7, with $k^{exp} = 0.63$ M^{-1} s^{-1}).

measurements of the palladium(0) oxidation currents (see Experimental Section and compare the potential scan shown in the insert in Figure 2a). The current measurements were then stable over periods exceeding the duration of any kinetics reported hereafter.

Kinetics of Oxidative Addition of Substituted Iodobenzenes to Pd(0) in Toluene. The kinetics of disappearance of zerovalent palladium in the presence of different concentrations of several substituted iodobenzenes were monitored by following the decay of the plateau current of the Pd(0) electrochemical wave as a function of time (see Figure 2a and Experimental Section). In a general case the current plateau decayed according to (compare Figure 2)

$$(i - i_\infty)/(i_0 - i_\infty) = (1 - [Pd^0]_0/[ArI]_0)/ \{\exp[k^{exp}([ArI]_0 - [Pd^0]_0)t] - [Pd^0]_0/[ArI]_0\} \quad (7)$$

where the subscripts 0 and ∞ indicate the values at zero and infinite times, respectively. Equation 7 corresponds to the simple rate law in eq 8, i.e. to an overall second-order process, first order in zerovalent palladium and first order in iodobenzene.

$$v = -d[Pd^0]/dt = k^{exp}[ArI][Pd^0] \quad (8)$$

Least-squares regression based on the general rate law in eq 7 allowed the experimental rate constant, k^{exp}, to be determined as a function of the triphenylphosphine concentration. A strict inverse proportionality of k^{exp} vs $[PPh_3]$, i.e. $k^{exp} = k_0^{exp}/[PPh_3]$, is obtained (see Figure 3a), indicating a complex rate law identical with that previously reported in THF:[8a]

$$v = -d[Pd^0]/dt = k_0^{exp}[ArI][Pd^0]/[PPh_3] \quad (9)$$

Arrhenius plots of k_0^{exp} over the 20–50 °C temperature range afforded straight lines, as shown in Figure 3b. Thus, $\Delta H^*(exp) = 75 \pm 5$ kJ mol^{-1} and $\Delta S^*(exp) = 7 \pm 5$ J mol^{-1} K^{-1}[32] were determined for iodobenzene. The rate constants k_0^{exp} measured at 25 °C for a series of para-substituted iodobenzenes follow a good Hammett correlation with $\rho = 2.3 \pm 0.2$, as evidenced by the plot in Figure 4. No attempt was made to obtain data for bromo- or chlorobenzenes, which are considerably less reactive.

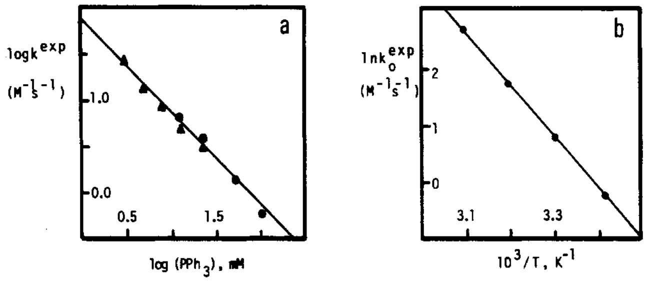

Figure 3. Experimental dependences of (a) k^{exp} on the triphenylphosphine concentration and (b) k_0^{exp} on the temperature, for the reaction of $Pd^0(PPh_3)_4$ (1.5 mM) with iodobenzene in toluene, 0.06 M $NHex_4BF_4$: (a) 3 mM (▲) and 10 mM (●) PhI, 25 °C; (b) 50 mM PPh_3, 3–10 mM PhI.

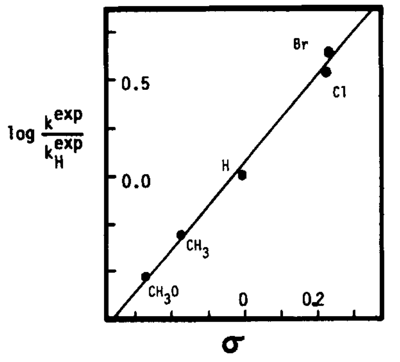

Figure 4. Hammett correlation for the reaction of $Pd^0(PPh_3)_4$ (1.5 mM) with substituted *p*-iodobenzenes (10 mM) in the presence of PPh_3 (50 mM) in toluene, 0.06 M $NHex_4BF_4$.

Discussion

The above results demonstrate the great advantages of electrochemistry at ultramicroelectrodes for monitoring reactions in solvents with extremely low dielectric constants. Kinetic data may then be obtained via amperometric methods at ultramicroelectrodes in media very similar to those used in organic and organometallic chemistry. As such, the method is a valuable complement to spectrometric ones, for cases such as the one presented in this study, where for example UV–visible techniques are difficult or impossible to use.

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[32] In the evaluation of $\Delta S^*(exp)$, the preexponential factor was assumed to be equal to kT/h, to allow a comparison of our results with those in ref 8a.

The oxidative addition of substituted iodobenzenes to zerovalent palladium in toluene corresponds to the overall rate law in eq 9, which involves first-order dependences with iodobenzene and palladium and an inverse first-order dependence with the triphenylphosphine ligand. No deviation from eq 9 was observed even at low phosphine concentration,[33] provided that the "free" phosphine concentration was corrected by considering that the first dissociation equilibrium in eq 10 was totally displaced.

$$Pd^0(PPh_3)_4 \rightleftharpoons Pd^0(PPh_3)_3 + PPh_3 \quad K_1 \qquad (10)$$

$$Pd^0(PPh_3)_3 \rightleftharpoons Pd^0(PPh_3)_2 + PPh_3 \quad K_2 \qquad (11)$$

$$Pd^0(PPh_3)_2 + ArI \rightarrow Ar\text{-}Pd^{II}I(PPh_3)_2 \quad k \qquad (12)$$

The initial palladium concentration being in the millimolar range, this implies that $K_1 \gg 10^{-3}$ M. Therefore, the experimental rate law in eq 9 necessarily corresponds to the involvement of the fast endergonic ligand dissociation in eq 11, which acts as a rapid preequilibrium ($K_2 < 10^{-4}$ M[33]) to the very act of oxidative addition in eq 12. This is further confirmed by the almost negligible value found for $\Delta S^\ddagger$(exp). Indeed, the combination of the large positive thermodynamic component ΔS_2^0 due to a PPh_3 ligand dissociation (eq 11) and of the expected large negative activation component $\Delta S^\ddagger$ due to the associative reaction (eq 12)[12] results in an overall small value for the experimentally determined activation entropy $\Delta S^\ddagger$(exp). The reaction of oxidative addition of iodobenzene to $Pd^0(PPh_3)_2$ in toluene therefore follows a mechanism identical with that previously observed in THF.[8a] The identity of the two reactions is further confirmed by the nearly identical ρ values (2.0 in THF[8a] vs 2.3 ± 0.2 in toluene) obtained for Hammett correlations in the two solvents,[34] which indicate a similar distribution of charge density for the transition states pertaining to eq 12 in both solvents. This is in agreement with the almost identical values of the activation entropies (respectively 13 and 7 J mol^{-1} K^{-1} in THF and toluene) found in the two solvents.

Let us now discuss the implications of the striking identity of the activation enthalpies; $\Delta H^\ddagger$(exp) = 75 kJ mol^{-1} in toluene and $\Delta H^\ddagger$(exp) = 77 kJ mol^{-1} in THF. This corresponds to nearly identical activation barriers for the reaction of the coordinatively unsaturated $Pd^0(PPh_3)_2$ with iodobenzene in both solvents, as the equilibrium constant K_2 (eq 11) is considered to be rather insensitive to solvent changes.[18] Except for minor variations arising from expectedly small differences in the solvation of the neutral $Pd^0(PPh_3)_2$ species, this supposes that no solvent coordination is involved in eq 11. K_2 could not be determined in toluene ($K_2 \leq 1.5 \times 10^{-5}$ M in THF[17b]), and therefore, no direct quantitative argument can be used to validate the above assumption. However, several indirect arguments support this hypothesis. (i) K_1 is only slightly solvent-dependent,[18] which supports K_2 also being solvent-independent, except if solvent (S) coordination is involved, as for example in the sequence[35]

$$Pd^0(PPh_3)_3 + S \rightleftharpoons S\text{-}Pd^0(PPh_3)_2 + (PPh_3) \quad K_2' \qquad (11')$$

$$S\text{-}Pd^0(PPh_3)_2 + ArI \rightarrow Ar\text{-}Pd^{II}I(PPh_3)_2 + S \quad k' \qquad (12')$$

(ii) In that case, the striking identity between the experimental activation parameters in both solvents would then require that the possible large variations in K_2', i.e. of ΔH_2^0 or ΔS_2^0, are exactly compensated by identical large variations in $\Delta H^{\ddagger\prime}$ of $\Delta S^{\ddagger\prime}$. (iii) Besides invoking a mere coincidence, such a requirement is in contradiction with the almost identical Hammett slopes in both solvents, since this latter parameter is independent of K_2' (or K_2) and reflects only effects in k' (or k). Indeed, large changes in $\Delta H^{\ddagger\prime}$ or $\Delta S^{\ddagger\prime}$ should correspond to large differences in transition states and therefore to changes of the Hammett slopes.

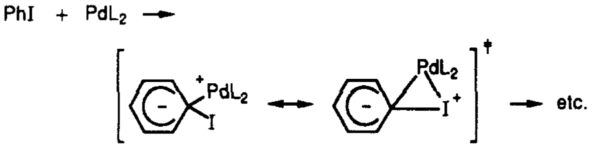
We thus consider likely that the zerovalent palladium species undergoing the very act of oxidative addition in eq 12 involves no solvent coordination.[35] At first sight this assumption may seem counterintuitive since 16- and 14-electron species are then involved. Yet, following previous authors,[1b,e,f,3,9,18] we believe that the creation of such a coordinatively unsaturated species is a prerequisite to the success of oxidative addition.[35] This species can be formed either by direct means, as in eq 11, or via a more complex sequence, as in eqs 11′ and 11″. However, because of

$$Pd^0(PPh_3)_3 + S \rightleftharpoons S\text{-}Pd^0(PPh_3)_2 + (PPh_3) \quad K_2' \qquad (11')$$

$$S\text{-}Pd^0(PPh_3)_2 \rightleftharpoons Pd^0(PPh_3)_2 + S \quad K_2'' \qquad (11'')$$

thermodynamic requirements (i.e. $K_2 = K_2'K_2''$), both sequences are kinetically equivalent as soon as reactions 11 or 11′ and 11″ are equilibrated, a fact established by the experimental rate law in eq 9.

Therefore, the identity of the activation parameters in both solvents favors, at least qualitatively, a transition state implying no charge development[4] and militates therefore against a reaction initiated by a single-electron transfer (i.e. path ii in Scheme I) or proceeding via a transition state analogous to that of nucleophilic aromatic substitution, as previously proposed for the reaction in THF[8a] or in benzene[8b] ($L = PPh_3$):



(13)

On a more quantitative basis, the activation enthalpy $\Delta H^\ddagger$ relative to the oxidative addition can be separated into two contributions: a "chemical" one, $\Delta H^\ddagger_{chem}$, corresponding to the partial bond breakings and creations in the transition state, and an "electrostatic" one, $\Delta H^\ddagger_{elec}$, corresponding to the solvation of the electrical dipoles in Scheme I (path ii)[4] or in eq 13, which corresponds to two elemental charges, $+e$ and $-e$, separated by a distance r. Provided that the mechanism of oxidative addition remains identical in both solvents investigated here (THF and toluene), important variations in $\Delta H^\ddagger$ should arise mainly because of the $\Delta H^\ddagger_{elec}$ contribution. Let us therefore estimate the magnitude of this latter value in both solvents for each transition state (in path ii in Scheme I or in eq 13).

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[33] This establishes that K_2 (eq 11) is considerably less than 10^{-4} M in toluene. Otherwise a constant term would be involved (compare eq 5 when $[L]^2 \ll K_1K_2$), and a strict inverse proportionality between k^{exp} in eq 8 and $[PPh_3]$ could not have been observed at low phosphine concentrations.

[34] (a) A similar value ($\rho = 2.0$) is reported in ref 9, p 6323, for oxidative addition of aryl iodides to $Ni^0(PEt_3)_3$ in hexane and THF. (b) However, a "two-slope" Hammett correlation ($\rho \approx 0$ for $\sigma < 0.2$; $\rho = 8.8$ for $\sigma > 0.2$) is also reported for oxidative addition of aryl halides to $Ni^0(PPh_3)_3$: Foà, M.; Cassar, L. *J. Chem. Soc., Dalton Trans.* **1975**, 2572.

[35] In this context it is worth mentioning that[15a] $Ni^0(dppe)_2$ is unreactive toward PhBr, although $Ni^0(PPh_3)_4$ and $Ni^0(PEt_3)_4$ undergo rapid reactions. In contrast, the electrogenerated, coordinatively unsaturated $Ni^0(dppe)$ reacts with PhBr with $k = 10^6$ M^{-1} s^{-1}, i.e. about 10^5 times faster than $Ni^0(PPh_3)_4$ and $Ni^0(PEt_3)_4$. This demonstrates that the inertness of $Ni^0(dppe)_2$ originates from the chelating properties of the dppe ligand, which oppose its dissociation prior to the oxidative-addition step. Therefore, a three-coordinate species such as $S\text{-}Pd^0(PPh_3)_2$, which is electron-poor as compared to $Pd^0(PPh_3)_3$, should be less reactive than the latter species in oxidative addition, except when the reaction proceeds via loss of the coordinated solvent (eqs 11′ and 11″).

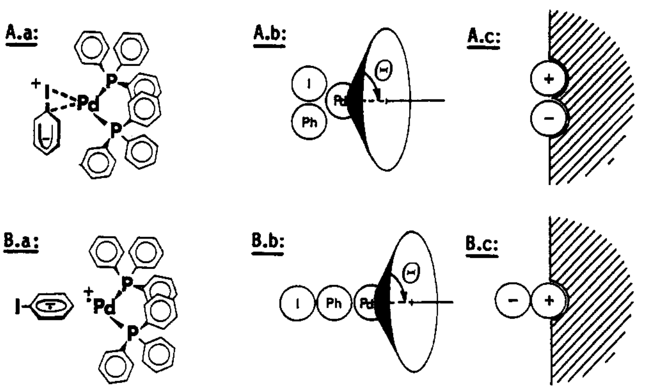

Figure 5. Schematic representation of the effect of the triphenylphosphine ligands on the solvation of two hypothetical ionic transition states, A (eq 15) and B (eq 14), for the reaction of $Pd^0(PPh_3)_4$ with iodobenzene (see text): (a) "chemical" representation of the transition state; (b) "spherical" representation and cone angle showing the space not available for solvation; (c) continuum models used for the derivation of eq 14 or 15, the hatched zone corresponding to the fraction of space not available for solvation.

Direct application of solvation theories, such as those derived from Born's model,[36a] to the cases investigated here is hampered by the fact that the two triphenylphosphine ligands of the palladium center hinder solvation of the dipole by the surrounding solvent. Molecular models show that approximately only half of the space is available to the solvent for solvation of the dipole (see Figure 5).[36b] Therefore, for the transition state corresponding to an electron-transfer mechanism (path ii in Scheme I), one has[37]

$$\Delta H^{\ddagger}_{\text{elec}}(1) \approx (7 \times 10^2/\epsilon_s) \times [1/a_{\text{Ph}} - 1/r + 0.5(1/a_{\text{Pd}} - 1/r)] + \text{cst} \quad (14)$$

where $\Delta H^{\ddagger}_{\text{elec}}$ is expressed in kJ mol^{-1} and the various radii and distances ($r \approx a_{\text{Ph}} + a_{\text{Pd}}$) are in Å. For the transition state represented in eq 13, one obtains by considering that now $r \approx a_{\text{Ph}} + a_{\text{I}}$[37]

$$\Delta H^{\ddagger}_{\text{elec}}(2) \approx (7 \times 10^2/\epsilon_s)0.5[1/a_{\text{Ph}} + 1/(a_{\text{I}} - 2/r)] + \text{cst}' \quad (15)$$

When we take $a_{\text{Ph}} = 2.5$ Å, $a_{\text{Pd}} = 1.3$ Å, and $a_{\text{I}} = 1.33$ Å and discard the constant terms,[37a] eqs 14 and 15 yield respectively $\Delta H^{\ddagger}_{\text{elec}}(1) = 270/\epsilon_s$ kJ mol^{-1} and $\Delta H^{\ddagger}_{\text{elec}}(2) = 220/\epsilon_s$ kJ mol^{-1}, showing that both transition states correspond to nearly identical solvation energies. Using $\epsilon_s = 7.58$ for THF and $\epsilon_s = 2.38$ for toluene then affords $\Delta H^{\ddagger}_{\text{elec}}(1, \text{THF}) \approx 35$ kJ mol^{-1} and $\Delta H^{\ddagger}_{\text{elec}}(1, \text{toluene}) \approx 115$ kJ mol^{-1} for a transition state corresponding to the electron-transfer mechanism (path ii in Scheme I). Such a transition state should therefore correspond to an increase of ca. 80 kJ mol^{-1} for the overall activation enthalpy, $\Delta H^{\ddagger}(\text{exp})$, as one passes from THF to toluene. This variation is clearly not compatible with the experimental observation of nearly identical values in both solvents. Similarly, the transition states in eq 13 would correspond to a variation of ca. 60 kJ mol^{-1} ($\Delta H^{\ddagger}_{\text{elec}}(2, \text{THF}) \approx 30$ kJ mol^{-1} and $\Delta H^{\ddagger}_{\text{elec}}(2, \text{toluene}) \approx 90$ kJ mol^{-1}), clearly too high to be compatible with the experimental results.

We are thus inclined to consider that the experimental transition state in eq 12 involves no charge development of the kind considered in eq 13 or in route ii of Scheme I. It must be recalled here that this conclusion rests in part on the hypothesis that K_2 in eq 11 is independent of the nature of the solvent, a fact that we consider as a likely assumption but could not establish quantitatively (vide supra). However, we think that this result should not be transposed without great caution to other metals or organic halides. For example, Tsou and Kochi[9a] examined the solvent dependence (hexane, toluene, THF) of the overall rate constant corresponding to the reaction of $Ni^0(PEt_3)_3$ with a series of substituted halobenzenes. They observed relatively large variations ($k^{\text{exp}}_{\text{THF}}/k^{\text{exp}}_{\text{toluene}} = 8.8$) for the experimental rate constant of oxidative addition with iodobenzene. Although these variations were not discussed in terms of their activation parameters, they are consistent with an ionic transition state, in agreement with the observation of paramagnetic nickel(I) halides as side products, whose formation was ascribed to the "cage-escape" pathway in eq 16b. Similar conclusions were obtained by Osborn and co-workers.[6,7]

$$\mathrm{Ni^0} + \mathrm{ArX} \longrightarrow [\mathrm{Ni^I}, \mathrm{ArX^{\bullet -}}] \begin{cases} \longrightarrow [\mathrm{Ni^I}, \mathrm{Ar^\bullet X^-}] + \mathrm{ArNi^{II}X} & (16a) \\ \longrightarrow \mathrm{Ni^+} + \mathrm{ArX^{\bullet -}} + \text{etc.} & (16b) \end{cases}$$

Such a difference, viz. a concerted pathway for zerovalent palladium and presumably an electron-transfer one for zerovalent nickel, may be related to a change of thermodynamics. The latter is, however, difficult to establish on clear grounds since up to now $E°$ values have not been available for coordinatively unsaturated zerovalent metals involved in oxidative addition. Indeed, electrochemical oxidation of, for example, $Pd^0(PPh_3)_2$[15a] or $Ni^0(dppe)$[15b] results in the observation of irreversible cyclic voltammograms. Therefore, the corresponding peak potential values ($E^p = +0.10$ V[15a] and -0.28 V[15b] vs SCE in THF for Pd^0L_2 and Ni^0L_2, respectively) include kinetic components in addition to purely thermodynamic ones.[22a,38] Nevertheless, the coordinatively unsaturated bis(triphenylphosphine)palladium(0) is oxidized at a potential ca. 0.38 V more positive than that for the related zerovalent nickel complex. On the basis of this value, an electron transfer from Pd^0L_2 to any organic halide should be ca. 35 kJ mol^{-1} more endergonic than from Ni^0L_2 to the same halide.[39] Such a result may explain the difference of the nature of oxidative additions to these two zerovalent metals, an electron-transfer mechanism being a priori more favorable

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(36) (a) For a general discussion of Born's model, see e.g. Bockris, J. O.; Reddy, A. K. N. In *Modern Electrochemistry*; Plenum Press: New York, 1977; Vol 1, pp 49–60. (b) Considering that only a half-space is available for solvation, we are possibly underestimating $\Delta H^{\ddagger}_{\text{elec}}$. Therefore, the variations of $\Delta H^{\ddagger}_{\text{elec}}$ with the solvent change are also underestimated. If a solid angle θ is forbidden to solvation, owing to the bulkiness of the palladium ligands, the factors 0.5 in eqs 14 and 15 should be replaced by θ/π.

(37) (a) The constant term cst (or cst′) in eq 14 (or 15) represents the electrical component due to the dipole interaction with the phosphine ligands. For an identical geometry of the transition state in different solvents, this term is independent of the solvent. These terms are therefore not included in the numerical evaluations of $\Delta H^{\ddagger}_{\text{elec}}(1 \text{ or } 2)$. (b) Compare to a similar expression obtained for the reorganization energy, λ_0, in Marcus' theory[13a] of outer-sphere electron transfer. (c) A reviewer suggested that ionic partners (supporting electrolyte) may be involved in an ionic transition state and should then be considered in the prediction of $\Delta H^{\ddagger}_{\text{elec}}(1 \text{ or } 2)$ in a nonpolar medium such as toluene, where ion pairing cannot be excluded. However, the participation of ionic partners in the activated complex is extremely unlikely. Indeed it would amount to a "three- or four-body" collision, since the reactants, being neutral, are not associated with ionic partners before the transition state. A second objection is that any specific stabilization by ion pairing of an hypothetical ionic activated complex is necessarily energetically compensated by the destabilization due to the dissociation of the former ion pair from which the ionic partner was issued. Compare Marcus's theory[13a] for a similar situation in electron-transfer reactions.

(38) For a discussion of this problem in organic systems, see e.g.: Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(39) Assuming that the variation in E^p parallels that of $E°$, one has $\delta(\Delta G°) \approx F(E^p_{\text{Pd(0)}} - E^p_{\text{Ni(0)}})$, where F is the Faraday constant.

for a zerovalent nickel than for $Pd^0(PPh_3)_2$, which is considered in this study.

Experimental Section

I. Chemicals. Toluene (Janssen) was distilled over sodium and stored under nitrogen. Tetra-*n*-hexylammonium fluoroborate was obtained by ion exchange from commercial tetra-*n*-hexylammonium bromide (Fluka) and sodium fluoroborate (Janssen).

Tetrakis(triphenylphosphine)palladium(0) was prepared according to Rosevear's method,[40] by reduction of Na_2PdCl_4 with $NaBH_4$ in the presence of excess triphenylphosphine. Substituted iodobenzenes were purchased from Aldrich, Janssen, and K&K and used as received except for iodobenzene and *p*-iodotoluene, which were distilled before use.

II. Electrochemical Apparatus. The three-electrode cell was homemade and was equipped with a double gasket for proper temperature control (±0.1 °C, controlled by a Lauda M3 thermostat). The temperature was measured in the solution within the cell. The counter electrode was a platinum gauze of ca. 1 cm^2 surface area, placed within a few millimeters of the working electrode tip. The reference electrode was a $Ag/Ag^+BF_4^-$ (0.1 M in toluene with 0.06 M n-Hex_4NBF_4). The working electrode was a gold disk (10-μm diameter) obtained by cross-section of a gold wire (Goodfellow) sealed in glass.[24] It was polished over 0.3-μm alumina before use and between runs. To increase the signal/noise ratio, the cell and potentiostat were enclosed in a Faraday cage, since nanoampere currents were measured. The temperature control water circuit was grounded to the Faraday cage to avoid transmission of electrical noise from the thermostat, which was placed outside the Faraday cage. The experiments were conducted according to standard vacuum-line techniques.

The potentiostat was homemade.[41] The wave function generator was an EGG-Parc 175 apparatus. The voltammograms (i vs E) were recorded on a digital oscilloscope (Nicolet 3091; 12 bits) and then transfered to a PC (Amstrad 1512) for further processing. Because electrode pollution occurred under constant anodic polarization, amperometry at a fixed potential could not be used. The wave function generator was thus used in a repetitive mode, with an asymmetric triangular wave form (scan rate ratio $v_{Ox}/v_{Red} = 1/10$). The potential was scanned between −2.7 and +0.2 V (vs the Ag^+/Ag electrode), but only the segment from −1.2 to +0.2 V gave useful data, since the reductive part of the potential scan was only needed to "refresh" the electrode (compare insert in Figure 2a). No attempt was made to understand the exact pollution/depollution mechanisms. Scan rates were adjusted for each kinetic run in order to record approximately 50 voltammograms over a 90–95% conversion range, as examplified by Figure 2.

III. Data Processing. Each reaction run gave a set of successive voltammograms. The plateau current of each of these was proportional to the instant concentration of $Pd^0(PPh_3)_4$. The apparent half-wave potential $E_{1/2}^{app}$ is related[21] to the true $E_{1/2}$ and to the uncompensated resistance of the solution by $E_{1/2}^{app} = E_{1/2} - R_u i_{1/2}$. When $E_{1/2}^{app}$ was plotted against $i_{1/2}$, for different concentrations of zerovalent palladium, straight lines were obtained (see Figure 1c) and $R_u \approx 270 \pm 20$ MΩ and $E_{1/2} = -0.53$ V vs Ag/Ag^+ could be determined from their slopes and intercepts at 20 °C. The ensuing values of R_u were further used to reconstruct "ohmic-drop-free" voltammograms, such as those represented in Figure 1b, by replotting the experimental current, i, as a function of $E + iR_u$. Logarithmic analysis[22a] of the corrected voltammograms afforded the value $\alpha = 0.45 \pm 0.05$ for the transfer coefficient corresponding to the two-electron oxidation wave[42] of $Pd^0(PPh_3)_4$.

For any potential, set on the plateau of the corrected voltammograms, a set of values of the current (i.e. concentration of palladium complex) corresponding to different time incrementations could be determined. The rate constant was computed for each such set of current–time data by a least-squares method (involving three unknowns: rate constant, initial time,[43] and current at infinite time[44]) based on the rate law in eq 7.

Acknowledgment. This work has been supported in part by the CNRS and ENS. Partial support from the MRES is also acknowledged.

Registry No. $Pd^0(PPh_3)_4$, 14221-01-3; $Pd^0(PPh_3)_2$, 31989-57-8; iodobenzene, 591-50-4; 4-bromoiodobenzene, 589-87-7; 4-chloroiodobenzene, 637-87-6; 4-methyliodobenzene, 624-31-7; 4-methoxyiodobenzene, 696-62-8.

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[40] Rosevear, D. T.; Stone, F. C. A. *J. Chem. Soc. A* **1970**, 119.

[41] Amatore, C.; Jutand, A.; Pflüger, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *218*, 361.

[42] For a slow electron transfer, involving n electrons, the steady-state electrochemical wave is given by[22a]

$$E = E_{1/2} + (RT/\alpha nF) \ln [(i_{lim}/i) - 1]$$

where i_{lim} is the plateau value of the wave and α the transfer coefficient.

[43] For slow kinetics, the initial time is that at which the iodobenzene solution is introduced in the cell containing the $Pd^0(PPh_3)_4$ solution. For fast kinetics, the mixing time of the two solutions resulted in a large uncertainty for the initial time, which was then obtained by regression analysis.

[44] Owing to the fixed number of i–E data points (2000) available in the memory of the numerical oscilloscope (Nicolet 3091) used in this study, the kinetics could be followed only to ca. 90–95% conversion, if reasonable accuracy was desired. Therefore, the data at infinite time were not recorded but were obtained with use of regression analysis.