Reversible Formation of a Cationic Palladium(II) Hydride $[HPd(PPh_3)_2]^+$ in the Oxidative Addition of Acetic or Formic Acid to Palladium(0) in DMF

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Keywords: Palladium / Formic acid / Acetic acid / Oxidative addition / Hydrido complex

The oxidative addition of acetic or formic acid to $Pd^0(PPh_3)_4$ in DMF affords a cationic palladium(II) hydride, [*trans*-$HPd(PPh_3)_2(DMF)]^+$, with acetate or formate as the counter anion. The two reactions are reversible. The equilibrium and kinetic constants of the oxidative additions have been determined.

Introduction

Many palladium-catalyzed reactions are initiated by the reaction of a palladium(0) complex with an acidic derivative.[1] Such reactions include: i) cycloisomerization of enynes,[1,2] ii) hydrocarbonylation and hydrocarboxylation of alkynes,[3] iii) isomerization of alkynes to 1,3-dienes,[1][2a] iv) hydrocarbonylation of aryl halides.[4] In all these reactions, the catalytic cycle is considered to be induced by a hydridopalladium complex formed by reaction of the palladium(0) complex and the acidic derivative.[1,5] This hydridopalladium complex undergoes *syn* addition to an alkyne (hydropalladation) which generates a vinylpalladium(II) complex, a key intermediate for further reactions. This reaction has been used for the synthesis of vinylpalladium(II) intermediates as an alternative to the oxidative addition of vinyl halides to palladium(0) complexes.[6] When the acidic derivatives are strong acids (e.g. HBF_4, HCl, CF_3CO_2H, HOTs), the hydridopalladium formation may be regarded as the protonation of basic Pd^0 to afford $HPdL_n^+$ complexes ($HPdL_3^+$ [7] or $HPdL_2S^+$,[8] S = solvent) [Equation (1)].

$$H^+ + Pd^0L_{n'} \rightarrow HPdL_n^+ + (n'-n)L \qquad (1)$$

The palladium may then be considered as either Pd^0 ligated by a proton or as Pd^{II} ligated by a hydride,[5] albeit that the very negative shift of the ^1H NMR signal is more indicative of a hydride linked to a palladium(II) center. This is why this reaction is also considered as an oxidative addition.[5]

When weak carboxylic acids are involved (e.g. acetic acid,[1,2,3a,3d] formic acid[3b]), the reaction is regarded as an oxidative addition, i.e., insertion of palladium(0) into the H−X bond [Equation (2)].[1,5]

$$HX + Pd^0L_{n'} \rightarrow HPd^{II}XL_n + (n'-n)L \qquad (2)$$

It is not clear whether the X anion remains ligated to the palladium(II) center or not. For example, for acetic acid, the palladium hydride was initially postulated as being $HPd(OAc)L_n$[2] but more recently as $HPdL_n^+$.[1] To date, none of these complexes have been characterized.[1]

$HPdXL_2$ intermediates are also formed in palladium-catalyzed Heck reactions involving aryl halides ArX,[9,10] as the product of a β-hydride elimination of the σ-organopalladium(II) halide complex, which also generates the arylated olefin. The base-promoted recycling of $HPdXL_2$ to Pd^0L_2, which completes the catalytic cycle, is considered as a reductive elimination, i.e., the reverse of the oxidative addition of HX to a Pd(0) complex. $HPdXL_2$ complexes are key intermediates in Heck reactions since re-addition of these complexes to the double bond after arylation is the origin of double bond isomerization.[9,10] In the presence of Ag^+ [11,12] or Tl^+ [13] cations able to capture the halide, a cationic complex $HPdL_2^+$ may also be formed when aryl triflates are used[14,15] due to the triflate anion's low affinity for palladium(II) complexes.[15,16] In such cases, re-addition of $HPdL_2^+$ to the olefin after arylation may not take place.[15] This is one explanation, among others, for the better regioselectivity generally observed when Heck reactions are performed under ionic conditions.[12,13]

In our attempts to define the mechanism of the palladium-catalyzed electro-hydrocarbonylation of aryl iodides to aryl aldehydes, performed in the presence of formic acid,[4] we established that the catalytic cycle was initiated by the reversible oxidative addition of formic acid to a palladium(0) complex to afford a cationic hydride complex $HPdL_2^+$ together with formate anions.[4] We now report some more details of this reaction and on its extension to acetic acid.

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1434−1948/00/0808−1855 $ 17.50+.50/0

Results and Discussion

Evidence for the Reversible Formation of a Cationic Palladium-Hydride $HPd(PPh_3)_2^+$ in the Oxidative Addition of Acetic or Formic Acid to $Pd^0(PPh_3)_4$ by Conductivity Measurements in DMF

The oxidative addition of acetic acid to $Pd^0(PPh_3)_4$ in DMF has been monitored at 25 °C by conductivity measurements. The conductivity κ of a solution of $Pd^0(PPh_3)_4$ (2 mM) increased after addition of n equivalents of acetic acid ($n > 1$) and reached a limit (Figure 1). This limiting value increased for values of n up to 100, but decreased in the presence of added PPh_3 (Figure 1).

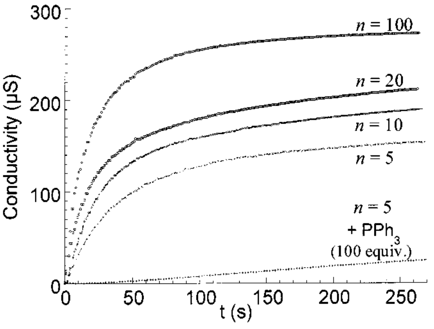

Figure 1. Conductivity measurements in DMF at 25 °C of a solution of $Pd^0(PPh_3)_4$ (2 mmol dm^{-3}) in the presence of n equivalents of acetic acid: n = 100, 20, 10, 5 in the absence of PPh_3 or in the presence of 100 equivalents of PPh_3 (when indicated)

Acetic acid is a weak acid in DMF (pK_a = 13.5).[17] Consequently, the concentration of the acetate anion and the proton is negligible compared to that of palladium(0) (2 mM). Their concentration was 8×10^{-5} mM when the acetic acid concentration reached 200 mM (n = 100). Nevertheless, the conductivity of acetic acid alone was first measured. It varied linearly with the square root of the acetic acid concentration, as expected for a weak acid. It varied from 1.7 to 6.9 µS when n was varied from 5 to 100 equivalents, respectively, so that the intrinsic conductivity of acetic acid was always negligible compared to that observed when acetic acid was added to $Pd^0(PPh_3)_4$ (Figure 1).

This series of experiments is evidence that the reaction of acetic acid and $Pd^0(PPh_3)_4$ affords ionic species which are involved in an equilibrium with the palladium(0) complex and acetic acid. PPh_3, whose overall effect is to decrease the concentration of the ionic species,[18] is then involved in the reverse reaction of this equilibrium. Since $Pd^0(PPh_3)_3$ is the major complex in solution [Equation (3)],[19] the observed overall equilibrium is described in [Equation (6)]. The inhibiting effect of PPh_3 strongly suggests that $Pd^0(PPh_3)_2$ participates in the reaction [Equations (4)−(5)], as in usual oxidative additions.[20] The mechanism of the oxidative addition of acetic acid to $Pd^0(PPh_3)_4$ may then be represented as in Equation (3) to (6) [reaction of $Pd^0(PPh_3)_4$ and acetic acid], in which the structure of the cationic complex has been established by spectroscopic techniques (vide infra).

$$Pd^0(PPh_3)_4 \rightleftharpoons Pd^0(PPh_3)_3 + PPh_3 \qquad (3)$$

$$Pd^0(PPh_3)_3 \rightleftharpoons Pd^0(PPh_3)_2 + PPh_3 \qquad (4)$$

$$Pd^0(PPh_3)_2 + CH_3CO_2H \rightleftharpoons HPd(PPh_3)_2^+ + CH_3CO_2^- \qquad (5)$$

Overall equilibrium:

$$Pd^0(PPh_3)_3 + CH_3CO_2H \overset{K}{\rightleftharpoons} HPd(PPh_3)_2^+ + CH_3CO_2^- + PPh_3 \qquad (6)$$

The reaction of $Pd^0(PPh_3)_4$ and formic acid was also monitored by conductivity measurements and led to similar results (Equation 7).[4]

However, the resulting solutions are less stable (the limiting value of the conductivity slightly increased with time) and the experiments have thus been performed at 0 °C. The equilibrium [Equation (7)] is fully displaced to the right-hand side in the presence of 70 equivalents of formic acid.

$$Pd^0(PPh_3)_3 + HCO_2H \overset{K}{\rightleftharpoons} HPd(PPh_3)_2^+ + HCO_2^- + PPh_3 \qquad (7)$$

The molar conductances ΛM have been calculated for the two complexes $[HPd(PPh_3)_2^+][CH_3CO_2^-]$ and $[HPd(PPh_3)_2^+][HCO_2^-]$ in DMF (Table 1). Their values are comparable to those reported for related complexes, e.g. $[HPd(PCy_3)_2(H_2O)^+][BF_4^-]$.[8]

Therefore, a cationic hydrido palladium(II) complex is formed by a reversible reaction starting from either acetic or formic acid.

Characterization of [*trans*-$HPd(PPh_3)_2(DMF)^+$][X^-] (X^- = $CH_3CO_2^-$, HCO_2^-)

Whereas neutral $HPdXL_2$ complexes have two coordinated phosphanes,[5] cationic palladium hydrides ligated by PPh_3 are usually characterized as three-coordinated complexes $HPdL_3^+$.[7e][7f] When cationic palladium hydrides are generated by the oxidative addition of acetic or formic acid to $Pd^0(PPh_3)_4$ in DMF, their ^{31}P NMR spectra exhibit a single signal for the ligated PPh_3 (Table 1) which is characteristic of a *trans* complex with two equivalent phosphorous, the fourth coordination site presumably being occupied by the solvent: *trans*-$HPd(PPh_3)_2(DMF)^+$. Despite the excess of PPh_3 from $Pd^0(PPh_3)_4$, the complex $HPd(PPh_3)_3^+$ is not formed in DMF. The solvent appears then to be a better ligand than a third PPh_3, presumably due to steric hindrance. This seems to be general since the oxidative addition of aryl triflates to $Pd^0(PPh_3)_4$ does not afford $ArPd(PPh_3)_3^+$, as is usually postulated, but *trans*-$ArPd(PPh_3)_2(DMF)^+$.[16]

The hydride has been characterized in both cases by its ^{1}H NMR signal, which has a negative chemical shift (Table 1).[21] The shifts of the ^{1}H and ^{31}P NMR signals for the two cationic complexes formed from either acetic acid or formic acid are very similar (Table 1) and do not depend significantly on the counter anion, acetate or formate, valid-

Table 1. Characterization of the cationic hydridopalladium(II) complex, $HPd(PPh_3)_2^+$ formed in the oxidative addition of $Pd^0(PPh_3)_4$ to acetic or formic acid in DMF (Equations 6 and 7)

$L = PPh_3$	Precursor	Molar conductivity (ohm^{-1} cm^2 mol^{-1})	H NMR (ppm)[a]	^{31}P NMR (ppm)[b]	E^p_{Red} (V)[c]	K/C_0[d]	k_f (M^{-1} s^{-1}) (k_b) (M^{-2} s^{-1})
$HPdL_2^+$	CH_3CO_2H	135[e] $[HPdL_2^+] + [CH_3CO_2^-]$	−7.48 (s)	20.77 (s)	−0.99[f] −0.85[g]	0.25 ± 0.01[e]	0.28[e] (560)[e]
$HPdL_2^+$	HCO_2H	110[h] $[HPdL_2^+] + [HCO_2^-]$	−7.28 (s)	20.97 (s)	−0.99[f]	0.5 ± 0.1[h]	0.012[h] (12)[h]

[a] 400 HMz; shifts are referred to TMS. Solvent: $CDCl_3$ containing 10% of DMF. − [b] 163 MHz, shifts are referred to H_3PO_4. Solvent: DMF containing 10% [D_6]acetone. − [c] Peak potentials in DMF are relative to SCE. Scan rate: 0.2 Vs^{-1} at 20 ° C. − [d] $C_0 = [Pd(PPh_3)_4]_0 = 2$ mM. − [e] 25 °C. − [f] At a carbon disk electrode. − [g] At a gold disk electrode. − [h] 0 °C. −

ating then the formulations used in Equation (6) and Equation (7).

Cyclic voltammetry, performed at a gold disk electrode, of a solution of $Pd^0(PPh_3)_4$, 2 mM in DMF (containing nBu_4NBF_4, 0.3 M) exhibits, at the gold electrode, the oxidation peak O_1 of $Pd^0(PPh_3)_3$ at + 0.057 V vs. SCE, whose peak current is proportional to the Pd^0 concentration (Figure 2a).[22]

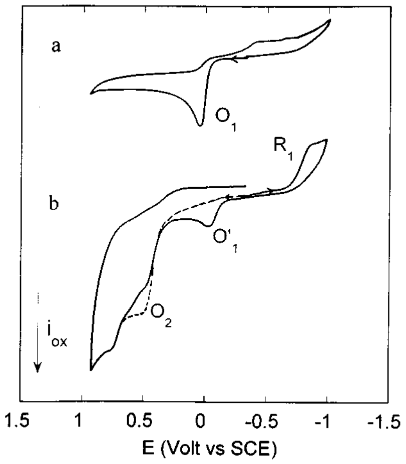

Figure 2. Cyclic voltammetry performed in DMF (containing nBu_4NBF_4, 0.3 mol dm^{-3}) at a steady gold disk electrode (0.5 mm diameter, scan rate: 0.2 V s^{-1}) at 20 °C: a) $Pd^0(PPh_3)_4$ (2 mmol dm^{-3}); b) $Pd^0(PPh_3)_4$ (2 mmol dm^{-3}) in the presence of 100 equivalents of acetic acid: (---) oxidation scan; (−) reduction scan performed first, followed by an oxidation scan

In the presence of 100 equivalents of acetic acid, the oxidation peak O_1 is no longer detected (Figure 2b, dashed voltammogram) indicating that the palladium(0) complex has undergone an oxidative addition reaction with acetic acid [Equation (6)]. The oxidation peak O_2 of the acetate anion is detected at +0.56 V. The voltammogram also exhibits a reduction peak R_1 at −0.85 V (Figure 2b, Table 1) which characterizes the reduction of the palladium(II) hydride complex formed in the oxidative addition. This reduction affords a palladium(0) complex, detected on the reverse scan by its oxidation peak O'_1 at −0.030 V (Figure 2b). Since acetate is the counter anion of the cationic palladium hydride, the reduction of $HPd(PPh_3)_2^+$ affords an anionic $Pd^0(PPh_3)_2(OAc)^-$ complex [Equation (8)].[23]

$$HPd(PPh_3)_2^+ + AcO^- + 1e \longrightarrow Pd^0(PPh_3)_2(OAc)^- + \tfrac{1}{2} H_2 \qquad (8)$$

The voltammetric investigation of $Pd^0(PPh_3)_4$ in the presence of 100 equivalents of formic acid gives identical results[4] (Table 1). Whatever the precursor, acetic acid or formic acid, the same reduction peak R_1 is observed (Table 1), confirming that the same palladium hydride complex is formed in the oxidative addition of $Pd^0(PPh_3)_4$ to either acetic or formic acid [Equations (6) and (7)].

Determination of the Equilibrium and Kinetic Constants of the Oxidative Addition of $Pd^0(PPh_3)_4$ to Acetic or Formic Acid

The oxidative addition of acetic acid or formic acid to $Pd^0(PPh_3)_4$ obeys Equation (9). The equilibrium constant has been determined from the conductivity data (Figure 1).

$$Pd^0L_3 + HX \overset{K}{\rightleftarrows} HPdL_2^+ + X^- + L \qquad (9)$$

$L = PPh_3$; $HX = CH_3CO_2H, HCO_2H$

Denoting x_{eq} as the equilibrium concentration ($t > 250$ s) of $HPdL_2^+$ and X^- relative to the initial concentration C_0 of $Pd^0(PPh_3)_3$, one gets [Equation (10)]:

$$K = \frac{[HPdL_2^+][X^-][L]}{[PdL_3][HX]} \qquad \frac{K}{C_0} = \frac{(x_{eq})^2(1+x_{eq})}{(1-x_{eq})(n-x_{eq})} \qquad (10)$$

$x_{eq} = \kappa_{eq}/\kappa_{irrev}$; κ_{eq} = conductivity measured when the equilibrium in Equation (9) is fully established in the presence of n equivalents of HX ($t > 250$ s); κ_{irrev} = conductivity when the equilibrium in Equation (9) is totally displaced towards its right-hand side, ($n = 100$ for CH_3CO_2H and HCO_2H, $t > 250$ s). The values of K/C_0 were then calculated for acetic and formic acid from Equation (10) (Table 1).

The rate constant of the overall forward reaction [k_f in Equation (13)] has been determined in the presence of 100 equivalents of HX, so that the reverse reaction is negligible (irreversible reaction as in the uppermost curve in Figure 1).

$$Pd^0(PPh_3)_3 \overset{K_0}{\rightleftarrows} Pd^0(PPh_3)_2 + PPh_3 \qquad (11)$$

$$Pd^0(PPh_3)_2 + HX \underset{k_-}{\overset{k_+}{\rightleftharpoons}} HPd(PPh_3)_2^+ + X^- \qquad (12)$$

$$Pd^0(PPh_3)_3 + HX \underset{k_b}{\overset{k_f}{\rightleftharpoons}} HPd(PPh_3)_2^+ + X^- + PPh_3 \qquad K \qquad (13)$$

Even under the conditions where the reaction in Equation (13) is irreversible, the PPh_3 released interferes in the mechanism through displacement of the equilibrium in Equation (11). If PPh_3 was in excess compared to $Pd^0(PPh_3)_4$, the kinetic law would simply be:
$\ln([Pd^0]_t/[Pd^0]_0) = -k_f[HX]t$
with $k_f = K_0k_+/[PPh_3]$. When starting from $Pd(PPh_3)_4$ alone, the concentration of PPh_3 is not constant [Equation (11)] and the kinetic law becomes:[22]
$2\ln([Pd^0]_t/[Pd^0]_0) - [Pd^0]_t/[Pd^0]_0 + 1 = -k_f[HX]t$
with $k_f = K_0k_+/C_0$. The value of k_f is then determined by plotting $2\ln(1 - x_t) + x_t$ *versus* time, up to 80% of conversion ($x_t = 1 - [Pd^0]_t/[Pd^0]_0$ with $x_t = \kappa_t/\kappa_\infty$; κ_t = conductivity at t; κ_∞ = final conductivity). k_f was calculated from the slope of the resulting regression line for acetic acid (Figure 3a) and formic acid (Figure 3b) (Table 1).

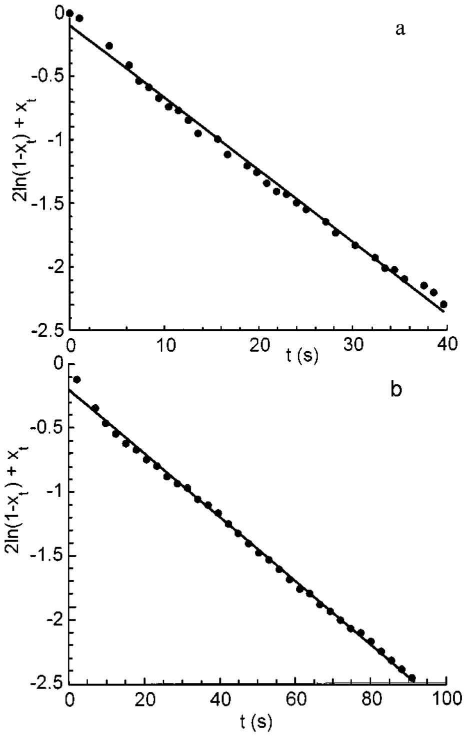

Figure 3. Kinetics of the oxidative addition of $Pd^0(PPh_3)_4$ (2 mmol dm^{-3} in DMF) under conditions where the reaction is irreversible, i.e.: a) acetic acid (0.2 mol dm^{-3}); b) formic acid (0.2 mol dm^{-3}); in both figures: plot of $2\ln(1 - x_t) + x_t$ *versus* time; $x_t = \kappa_t/\kappa_\infty$; κ_t = conductivity at t; κ_∞ = final conductivity

The value of the rate constant of the overall reverse reactions [k_b in Equation (13)] was then deduced from the equilibrium constant $K = k_f/k_b$ (Table 1).

Acetic acid is a weak acid in DMF. The concentration of the acetate anion and the proton are negligible (vide supra) compared to the palladium(0) concentration. However, this does not allow us to exclude direct protonation of $Pd^0(PPh_3)_2$. Discrimination between the two pathways: i) direct protonation of $Pd^0(PPh_3)_2$ by H^+ to form $HPdL_2^+$, or ii) oxidative addition of HX to $Pd^0(PPh_3)_2$ to form $H-Pd-XL_2$ followed by an ionization step, may be achieved by determination of the reaction order of HX under conditions where the equilibrium is totally shifted towards the cationic hydride complex (i.e. $n \geq 100$ equivalents for acetic acid, Figure 1). Indeed, a linear dependence of the observed rate constant on the acetic acid concentration would be in favor of an oxidative addition, whereas a linear dependence on the proton concentration, viz. with the square root of the acetic acid concentration, would be in favor of a protonation. The reaction of $Pd(PPh_3)_4$ with acetic acid is rather fast (Figure 1); consequently, only two concentrations of acetic acid could be tested ($n = 100$: $k_{obs} = 0.057\ s^{-1}$; $n = 200$: $k_{obs} = 0.104\ s^{-1}$). From these results, it ensues that the reaction order in acetic acid is close to unity, which is in favor of an oxidative addition of the $H-OAc$ bond to palladium(0). The intermediate neutral complex, $HPdXL_2$ (X = acetate or formate) does not accumulate in the solution, thus its ionization is faster than its formation. Indeed, the kinetic curves in Figure 1, as well as those we have reported for formic acid,[4] do not exhibit any induction period which would result in a significant accumulation of such a neutral species. The degradation observed at 25 °C, when the formate anion is the counter anion, probably arises from a side reaction induced by this anion. Indeed, the intermediate neutral $HPd(OCHO)L_2$ complex is prone to undergo a well-known decarboxylation reaction[24] with formation of $HPdHL_2$, leading to H_2 and Pd^0L_2.

Conclusion

Oxidative addition of acetic acid or formic acid to a palladium(0) complex in DMF affords a cationic palladium hydride *trans*-$HPd(PPh_3)_2(DMF)^+$, with an acetate or a formate counter-anion. Both reactions are reversible and involve an unfavorable equilibrium so that a large excess of acid is required for the quantitative formation of the palladium hydride complex. This work therefore provides confirmation of the assumption made by Trost in the conclusion of one of his latest papers on this topic: "Such a species [the palladium hydride] undoubtedly is formed to some extent [from weak acids], albeit in an unfavorable equilibrium".[1]

This allows us to conclude that the catalytic reactions initiated by reaction of palladium(0) and acetic acid (or formic acid) proceed via a cationic palladium hydride *trans*-$HPd(PPh_3)_2(DMF)^+$, when they are performed in DMF.

The relative values of the kinetic constants k_f and k_b show that $HPdL_2^+$ is easily converted back to a Pd^0 complex. This reverse reaction is the step which completes the catalytic cycle of Heck reactions when they are performed under ionic conditions (from aryl triflates[14,15,25] or aryl halides in the presence of Ag^+ or Tl^+ salts[11−13,25]) with $Pd(OAc)_2$ as the palladium(0) precursor or when acetate ions are used as a base.

Experimental Section

General Remarks: ^{31}P (101 MHz) and ^{1}H (400 MHz) NMR spectra were recorded on a Bruker spectrometer. Cyclic voltammetry was performed with a home made potentiostat and wave form generator Tacussel GSTP4. The cyclic voltammograms were recorded on a Nicolet 301 oscilloscope. Conductivities were measured on a Tacussel CDM210 conductimeter (cell constant: 1 cm^{-1}).

Chemicals: DMF was distilled from calcium hydride under vacuum and kept under argon. Acetic and formic acids were obtained commercially and used as pure compounds. Pd^{0}(PPh$_3$)$_4$ was synthesized according to a reported procedure.[26]

Electrochemical Set-Up and Electrochemical Procedure for Voltammetry: Experiments were carried out in a three-electrode cell connected to a Schlenk line. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area. The reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge filled with DMF (3 mL) containing nBu$_4$NBF$_4$ (0.3 M). DMF (12 mL) containing nBu$_4$NBF$_4$ (0.3 M) was introduced into the cell followed by Pd(PPh$_3$)$_4$ (28 mg, 0.024 mmol) and then 100 equivalents of acetic acid. Cyclic voltammetry was performed at a steady gold (0.5 mm diameter) or carbon (2 mm diameter) disk electrode at a scan rate of 0.2 V s^{-1}.

Acknowledgments

This work has been supported by the Centre National de la Recherche Scientifique (CNRS, UMR 8640), the Ministère de l'Education Nationale et de la Recherche et de la Technologie, and The Consiglio Nazionale delle Ricerche (CNR). Two undergraduate students T. Huy Lap and M. F. Perriot are thanked for their involvement in some of the experiments described in this work.

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Received March 1, 2000
[I00078]