

Kinetic Data on the Synergetic Role of Amines and Water in the Reduction of Phosphine-Ligated Palladium(II) to Palladium(0)

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Tertiary amines such as $EtN(iPr)_2$ do not reduce $[PdCl_2-(PPh_3)_2]$ into a Pd⁰ complex. The latter is formed only after the addition of water (generation of HO⁻), as was reported by Grushin and Alper for NEt₃. The mechanism of the Pd^{II}/Pd⁰ reduction performed in the presence of an excess amount of PPh₃ is established quantitatively by means of electrochemical techniques that provide kinetic data (determination of the equilibrium and rate constants) for the disappearance

Introduction

Many reactions performed from aryl halides ArX involve $[Pd^{II}X_2(PPh_3)_2]$ (X = halide, OAc) as precatalysts and a tertiary amine as a base.^[1] A Pd⁰ complex must be formed to activate ArX by oxidative addition. It is often considered that the Pd^{II} precatalyst is reduced in situ by tertiary amines to generate the Pd⁰ catalyst active in the catalytic reactions.^[2] In this respect, amines with a hydrogen in the α position with regard to the N atom (i.e., in a β position with regard to the Pd atom once the amine is ligated to the Pd^{II} center) were proposed to undergo β-hydride elimination ultimately to lead to a Pd⁰ complex via a HPdX intermediate.^[2] This was supposed to happen in Heck reactions [precatalyst: $Pd(OAc_2) + nPPh_3$], until it was established in 1992 by some of us that amines did not play any reducing role in the presence of a phosphine ligand.^[3a,3b] The same reduction process was later on reported by Ozawa, Kubo, and Hayashi in the presence of NEt₃ and water.^[4] However, the amine is not required.^[3b] Indeed, phosphine is the unique reducing agent that is able to reduce Pd(OAc)₂ to a Pd⁰ complex through a rate-determining reductive elimination step occurring in [Pd(OAc)2- $(PR_3)_2$] (R = Ar, alkyl) between OAc and the ligated PPh₃

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of $[PdCl_2(PPh_3)_2]$ and the formation of $[Pd^0(PPh_3)_3]$. $[PdCl(OH)(PPh_3)_2]$ is formed, which allows reductive elimination between OH and the ligated PPh₃ (zero-order reaction for PPh₃), and this leads to a Pd⁰ complex. The reducing agent is ligated PPh₃, which ultimately yields (O)PPh₃. The rate of the overall reduction process is controlled by the amount of water that imposes the concentration of HO⁻.

(zero-order reaction for PPh₃, Scheme 1). Phosphine oxide was generated in the presence of water,^[3a,3b] the concentration of which did not affect the kinetics of the reduction process (see Figure 2 in ref.^[3a]) because the hydrolysis takes place after the rate-determining reductive elimination step (rate constant $k_{\rm re}$) in which Pd⁰ is formed (Scheme 1).



Scheme 1. Mechanism of the reduction of $[Pd(OAc)_2(PPh_3)_2]$ to $Pd^{0}.^{[3a,3b]}$

Water is however required in the case of bidentate P^P ligands such as 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap), as reported by Osawa and Hayashi,^[4] and 1,3-bis(diphenylphosphino)propane (dppp), as reported by our group.^[3f] Indeed, owing to the bidentate character of P^P ligands, the O–P reductive elimination step that takes place in [Pd(OAc)₂(P^P)] is reversible, and the equilibrium needs be shifted towards the Pd⁰ complex by hydrolysis of the hemiphosphonium (see Schemes 3 and 4 in ref.^[3f]). Amines do not play any kinetic role in this reduction process.^[3f]

Grushin and Alper reported in 1993 that [PdCl₂(PPh₃)₂] was reduced to "Pd metal" in the presence of hydroxide ions (NaOH), whereas PPh₃ was oxidized to OPPh₃.^[5] These authors also observed that no Pd⁰ was formed in the presence of the dry amine NEt₃, whereas it was formed after the addition of water^[5] owing to the formation of HO⁻. The mechanism proposed by these authors considers the

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initial formation of $[PdCl(OH)(PPh_3)_2]$ leading to $[HPdCl(PPh_3)]$, the latter of which is responsible for the formation of Pd⁰ after reductive elimination of HCl. However, in our view, the inner-sphere situation in $[PdCl(OH)(PPh_3)_2]$ is similar to that occurring in $[PdCl(OAc)_2(PPh_3)_2]$ (Scheme 1). On the basis of this analogy, we expected that $[PdCl(OH)(PPh_3)_2]$ could directly evolve into a Pd⁰ moiety through a single step occurring within the palladium coordination shell through inner-sphere oxidation of one phosphine by hydroxy transfer. Given that the authors did not produce any kinetic data to firmly validate their postulated

mechanism, we decided to fully investigate the kinetics of the reduction of $[PdCl_2(PPh_3)_2]$ if the dry tertiary amine $EtN(iPr)_2$ and water were simultaneously present. Indeed, the exact mechanism involved for the overall reduction of the Pd center may have important consequences on the loading of the Pd⁰ catalyst and consequently on the rate and success of the catalytic reaction.

Results and Discussion

All reactions were performed in the presence of PPh₃ {3 equiv. with respect to $[PdCl_2(PPh_3)_2]$ (1)} to follow the kinetics of the formation of stable complex [Pd⁰(PPh₃)₃]^[6] (instead of palladium metal^[5]). Cyclic voltammetry was used to monitor the evolution of $[PdCl_2(PPh_3)_2]$ (C₀ = 2 mm) in dry DMF in the presence of dry $EtN(iPr)_2$ (2) and known amounts of H₂O at room temperature. Indeed, complex 1 is well characterized by cyclic voltammetry (CV) by its reduction peak at $E^{p}_{red} = -0.92$ V versus the saturated calomel electrode (SCE),^[7] and interestingly, its reduction peak current is proportional to its concentration at any time.^[8] If a reaction took place, the reduction peak current of 1 should decrease with time and the oxidation peak of resulting [Pd⁰(PPh₃)₃] (3) should appear concomitantly. The latter is indeed well characterized by its oxidation peak at $E^{p}_{ox} = -0.03$ V versus SCE with an oxidation peak current proportional to its concentration at any time.^[6] It was first checked that no Pd⁰ complex was formed after the addition of an excess amount of PPh₃ to 1, even over long reaction times. Thus, free PPh_3 did not reduce 1 to 3 at room temperature. No Pd⁰ was formed from [PdCl₂(PPh₃)₂] in the presence of 2 even in large amounts and at long times (Scheme 2).

$$\begin{array}{c|c} PdCl_{2}(PPh_{3})_{2}+3\ PPh_{3} & \longrightarrow \\ PdCl_{2}(PPh_{3})_{2}+3\ PPh_{3}+EtN(iPr)_{2} & \longrightarrow \\ PdCl_{2}(PPh_{3})_{2}+3\ PPh_{3}+H_{2}O & \longrightarrow \\ PdCl_{2}(PPh_{3})_{2}+3\ PPh_{3}+EtN(iPr)_{2}+H_{2}O & \longrightarrow \\ Pd^{0}(PPh_{3})_{3} & 1 & 2 & 3 \end{array}$$

Scheme 2.

It was only after addition of water that $[PdCl_2(PPh_3)_2]$ progressively disappeared, as attested by the decay in its reduction peak current with time (Figure 1, a). Furthermore, $[Pd^0(PPh_3)_3]$ was formed and detected by its oxi-

dation peak when CV was performed directly towards oxidation potentials. Its oxidation peak current increased with time (Figure 1, b). Consequently, a Pd⁰ complex was formed in situ from 1 in the presence of EtN(*i*Pr₂) only if water was added to [PdCl₂(PPh₃)₂] (Scheme 2), as observed by Grushin and Alper for NEt₃.^[5] Conversely, no Pd⁰ was formed in the presence of water and absence of amine (Scheme 2).



Figure 1. (a) Voltammetry of $[PdCl_2(PPh_3)_2]$ (2 mM) in DMF (15 mL, nBu_4NBF_4 , 0.3 M) at a gold disk electrode (d = 1 mm) at a scan rate of 0.5 V s⁻¹ performed in the presence of PPh₃ (6 mM), EtN(iPr_{2} (0.5 mL), and H₂O (1 mL) as a function of time at room temperature. (b) Oxidation of $[Pd^0(PPh_3)_3]$ generated in situ from $[PdCl_2(PPh_3)_2]$ as a function of time in the same reaction as that in (a).

The kinetics of the decay of 1 (2 mM) in the presence of 2 (0.5 mL, 100 equiv. with respect to 1) and H₂O (1 mL, 1852 equiv. with respect to 1) was monitored by chronoamperometry at a rotating disk electrode (RDE) polarized at -1.2 V on the reduction wave of [PdCl₂(PPh₃)₂]. The decreasing reduction plateau current of [PdCl₂(PPh₃)₂], proportional to its concentration, was recorded with time just after the addition of water (Figure 2, a).^[9]

In another experiment performed at the same concentrations, the kinetics of the formation of the Pd^0 complex was monitored by the same technique, and the RDE was polarized at +0.2 V on the oxidation wave of $[Pd^0(PPh_3)_3]$ (proportional to its concentration) was recorded with time just after the addition of water. Figure 2 (b) displays the concomitant evolution of the molar fractions of the Pd^{II} and Pd^0 complexes.

The plot of ln x versus time is linear (Figure 2, c) ($x = [1]_t/[1]_0 = i_t/i_0$; i_t = reduction current of 1 at t, i_0 = initial reduction current of 1) with ln $x = -k_{obs}^{Pd^{II}}t$. The plot of ln x' versus time is linear { $x' = ([3]_{fin} - [3]_t)/[3]_{fin} = (i_{fin} - i_t)/i_{fin}$; i_t = oxidation current of 3 at t, i_{fin} = final oxidation current of 3} with ln $x' = -k_{obs}^{Pd^{II}}t$ (Figure 2, d). The values of $k_{obs}^{Pd^{II}}$ and $k_{obs}^{Pd^{0}}$, determined from the slope of the straight lines in Figure 2 (c, d) respectively, were almost identical (Table 1, entries 3 and 4) upon considering the fact that $k_{obs}^{Pd^{II}}$ and $k_{obs}^{Pd^{0}}$ were independently determined in two different experiments (see above). Thus, $[PdCl_2(PPh_3)_2]$ disappeared (rate characterized by $k_{obs}^{Pd^{II}}$) at the same rate as $[Pd^0(PPh_3)_3]$ was formed (rate characterized by $k_{obs}^{Pd^{II}}$), which suggests that no intermediate complex accumulated during the reduction process. Importantly, the concentra-



Figure 2. Kinetics of the reduction of $[PdCl_2(PPh_3)_2]$ (1, 2 mM) to $[Pd^0(PPh_3)_3]$ in the presence of $EtN(iPr)_2$ (0.5 mL), water (1 mL), and PPh₃ (6 mM) in DMF (15 mL) at 25 °C. (a) Decay of the reduction plateau current of $[PdCl_2(PPh_3)_2]$ at a RDE (d = 2 mm) polarized at -1.2 V vs. SCE vs. time. (b) Evolution of the molar fraction of $[PdCl_2(PPh_3)_2]$ and $[Pd^0(PPh_3)_3]$ vs. time. (c) Kinetics of the decay of $[PdCl_2(PPh_3)_2]$: plot of ln *x* vs. time.

tion of PPh₃ did not affect the kinetics of the reduction process: $t_{1/2} = 112$ and 109 s in the presence of 3 and 6 equiv. of PPh₃ respectively, for reactions performed in the presence of **2** (0.5 mL) and H₂O (1 mL) (Figure S1, Supporting Information). Consequently, the Pd⁰ complex was formed in an intramolecular process (zero-order reaction for PPh₃) and the free PPh₃ was not the reductant.

Table 1. Observed rate constant $k_{obs}^{Pd^{II}}$ for the disappearance of $[PdCl_2(PPh_3)_2]$ and $k_{obs}^{Pd^0}$ for the formation of $[Pd^0(PPh_3)_3]$ in the in situ reduction of $[PdCl_2(PPh_3)_2]$ (2 mM) into $[Pd^0(PPh_3)_3]$ in the presence of $EtN(iPr)_2$ and water.^[a]

Entry	EtN(<i>i</i> Pr) ₂ /mL (equiv.)	H ₂ O /mL (equiv.)	$k_{\rm obs}^{\rm Pd^{II}} (k_{\rm obs}^{\rm Pd^0}) / {\rm s}^{-1}$
1	0.05 (10) ^[b]	0.5 (926) ^[b]	slow
2	0.5 (100) ^[b]	0.5 (926) ^[b]	1.4×10^{-3}
3	0.5	1	$3.1 \times 10^{-3[c]}$
4	0.5	1	$(3.6 \times 10^{-3})^{[c]}$
5	1.0	0.5	1.5×10^{-3}
6	1.0	1	2.5×10^{-3}

[a] All reactions were performed in the presence of PPh₃ (3 equiv.) in DMF (15 mL) at 25 °C. [b] Equiv. with respect to $[PdCl_2-(PPh_3)_2]$. [c] Determined in a separate series of experiments (see text).

The crucial role of water upon using an amine involves the reversible formation of hydroxide ions [Scheme 3, Equation (1)] with the formation of $[PdCl(OH)(PPh_3)_2]$ [4; Scheme 3, Equation (2)].^[5] By analogy with the well-established evolution of $[Pd(OAc)_2(PPh_3)_2]$ toward a Pd⁰ complex through O–P reductive elimination (Scheme 1),^[3a,3b] and the zero-order reaction found for PPh₃, one concludes

that the Pd⁰ complex is formed by a O–P reductive elimination between OH and ligated PPh₃ in 4 [Scheme 3, Equation (3)]. The *cis* coordination of these two groups favors reductive elimination. Therefore, ligated PPh₃ played the

role of reducing agent. Phosphine oxide, (O)PPh₃, ultimately formed in a fast reaction from HO–PPh₃⁺ (Scheme 3), was characterized by ³¹P NMR spectroscopy in DMF (121 MHz, H₃PO₄) as a singlet at $\delta = 25.4$ ppm.



Scheme 3. Mechanism for the reduction of $[PdCl_2(PPh_3)_2]$ to $[Pd^0(PPh_3)_3]$ in the presence of a tertiary amine and water from kinetic data.

Alper and Grushin analyzed their reaction (NEt₃ as the amine) by ³¹P NMR spectroscopy when the Pd^{II} was ligated by a chiral phosphine.^[5] Retention was observed at the P center in the isolated chiral phosphine oxide; they concluded that "the Pd^{II} phosphine complexes [...] are reduced to a Pd(⁰) species [...] not by extra phosphine, but by their own coordinated phosphine ligands which are oxidized to phosphine oxides, with OH playing the role as the specific promoter".^[5] The role of the ligated phosphine in the reduction process is confirmed from our kinetic data. Most importantly, the present kinetics evidence that the reduction is zero-order in phosphine, which disproves the involvement of a hydrido [HPdCl(PPh₃)]^[5] intermediate on the way to Pd⁰. Furthermore, this establishes on a sound kinetic basis that the entire two-electron reduction of the Pd center occurs directly within the [Pd(OH)Cl(PPh₃)₂] inner-sphere shell, that is, involving direct transfer of the hydroxy onto phosphorus with simultaneous formation of one [ClPd⁰(PPh₃)]⁻ and [HO–PPh₃]⁺ [Scheme 3, Equation (3)] in a perfectly analogous manner to that established previously by us for the palladium acetate case (Scheme 1). Hence, in both cases the oxidation state of the Pd center readily changes from II to 0, whereas that of the P center simultaneously goes from III to V through the formation of a [RO– PPh_3 ⁺ (R = H or Ac) intermediate.

The effect of the concentration of H_2O on the rate of formation of **3** was then investigated by maintaining a constant concentration of amine **2** in the presence of various amounts of H_2O . From the determination of k_{obs} (Table 1, entries 2, 3, 5, and 6; see also Figures S2–S5), it was observed that the higher the concentration of water, the faster the reaction (with a first-order reaction for H_2O , Figure S5), in agreement with a higher concentration of hydroxides formed in Equation (1), as this shifts the equilib-

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rium [Equation (2)] towards complex 4. The effect of the concentration of amine 2 was then investigated by maintaining a constant concentration of H_2O (Table 1, entries 2 and 5). The higher the concentration of amine, the faster the reaction at low H_2O concentrations, in agreement with a higher concentration of hydroxides formed in Equation (1).

The exact kinetic law that takes into account the fact that the kinetics were not investigated under pseudo-first-order conditions for Cl^- and $EtN(iPr)_2H^+$ was determined:

 $\ln x - 2x + 0.5x^{2} + 1.5 = -K_{\rm OH}K_{\rm Cl}k_{\rm re}[2][{\rm H}_{2}{\rm O}]t/2C_{0}^{2}$

The value of $K_{\text{OH}}K_{\text{CI}}k_{\text{re}} = 9.2 \times 10^{-9} \text{ s}^{-1}$ (DMF, 25 °C) was determined from the plot of $\ln x - 2x + 0.5x^2 + 1.5$ versus time (Figure S6).

No kinetic data was published by Grushin and Alper for the reduction of $[PdCl_2(PPh_3)_2]$ (1) to "Pd metal" in the presence of pure hydroxide ions (introduced via NaOH).^[5] In the present work, the reactions were performed in the presence of PPh₃ (3 equiv. vs. 1). The electrochemical technique (i.e., RDE) was used to follow the disappearance of $[PdCl_2(PPh_3)_2]$ ($C_0 = 2 \text{ mM}$) and the formation of $[Pd^0(PPh_3)_3]$ in the presence of NaOH (3.3 equiv., from a mother solution 1 M in water). Once more, stable $[Pd^0-(PPh_3)_3]$ was formed at the same rate as the Pd^{II} complex disappeared (Figure 3), which indicates that the reductive elimination [Scheme 4, Equation (3')] was rate determining, controlled by the equilibrium in Equation (2) (Scheme 4).



Figure 3. Kinetics of the reduction of $[PdCl_2(PPh_3)_2]$ (1, 2 mM) to $[Pd^0(PPh_3)_3]$ in the presence of NaOH (6.6 mM, 0.1 mL from a mother solution of NaOH, 1 M in water) and PPh₃ (6 mM) in DMF (15 mL) at 25 °C. (a) Decay of the molar fraction of $[PdCl_2-(PPh_3)_2]$ vs. time. (b) Increase in the molar fraction of $[Pd^0(PPh_3)_3]$ (3) generated in situ vs. time.

The half-reaction time for the formation $[Pd^{0}(PPh_{3})_{3}]$ was $t_{1/2} = 7.8$ s (Figure 3). This value can be compared to $t_{1/2} = 140$ s obtained in the presence of $EtN(iPr)_{2}$ (0.5 mL, 100 equiv.) and water (1 mL, 1852 equiv.; Figure 2, d). Even in the presence of a small amount of purposely added hydroxide ions, the reduction process was much faster because the equilibrium in Equation (1) in Scheme 3 was bypassed.

The kinetic law was determined^[10] and allowed the calculation of $K_{\rm Cl}k_{\rm re} = 2.6 \times 10^{-3} \, {\rm s}^{-1}$ (Figure S7). From the determination of $K_{\rm CH}K_{\rm Cl}k_{\rm re} = 9.2 \times 10^{-9} \, {\rm s}^{-1}$ (see above), one esti-



Scheme 4. Mechanism for the formation of $[Pd^0(PPh_3)_3]$ from $[PdCl_2(PPh_3)_2]$ in the presence of hydroxide in DMF from kinetic data.

mates the value of $K_{\rm OH} = 3.5 \times 10^{-6}$ (DMF, 25 °C; Scheme 3, Equation (1)].

All previous reactions were performed in dry DMF in the presence of dry $EtN(iPr)_2$. Some experiments were performed in nondistilled DMF in the presence of the nondistilled amine. The CV of [PdCl₂(PPh₃)₂] (2 mM) still performed in the presence of PPh_3 (3 equiv.) but in the absence of added water revealed that some $[Pd^{0}(PPh_{3})_{3}]$ was already formed in situ, which was detected by its oxidation peak. Again, addition of water greatly increased the rate of formation of the Pd⁰ complex. Consequently, in the absence of purposely added water, [PdCl₂(PPh₃)₂] could be transformed into a Pd⁰ complex in the presence of an amine via hydroxides generated by residual water. The rate of the reduction process was slow and was controlled by the low concentration of residual water. Addition of water accelerated the formation of the Pd⁰ complex. Whatever the case, the phosphine ligand remains the reducing agent by an intramolecular reduction process established by kinetic data (Scheme 3).

Conclusions

In conclusion, tertiary amines do not reduce [PdCl₂(PPh₃)₂] to a palladium(0) complex, even those possessing a hydrogen in the α position. It is only in the presence of H₂O that a Pd⁰ complex is formed; this confirms the previous work by Grushin and Alper.^[5] The mechanism for the reduction process is now quantitatively established with the determination of the equilibrium and rate constants thanks to electrochemical techniques that provided kinetic data on the concomitant formation of the Pd⁰ complex and the disappearance of the Pd^{II} complex during the reduction process. The synergetic role of amine and water only involves the formation of hydroxide ions in water to deliver [PdCl(OH)(PPh₃)₂], which allows the formation of a Pd⁰ complex through reductive elimination between ligated PPh₃ and the OH ligand. Therefore, the reducing agent is ligated PPh₃, which leads to phosphine oxide. The rate of the reduction is controlled by the amount of water through

adjusting the concentration of the hydroxides. This is why such reactions are slower than those performed in the presence of pure hydroxide ions, whereas the reduction process is essentially the same. Consequently, in catalytic reactions performed with the use of tertiary amines and $[PdCl_2-(PPh_3)_2]$ as a precatalyst, it is recommended to add water to facilitate the in situ reduction of $[PdCl_2(PPh_3)_2]$ into the required Pd⁰ complex, the catalytic loading of which is thus made higher. The catalytic reactions become thus faster in the presence of water.^[11]

Experimental Section

General Procedure for the Kinetic Measurements of the Reduction of $[PdCl_2(PPh_3)_2]$ in the Presence of Amine and Water: The kinetic measurements were performed by chronoamperometry at a rotating gold disk electrode (d = 2 mm) with an angular velocity of 105 rad s⁻¹ in a cell (see the Supporting Information) containing DMF (15 mL, with nBu_4NBF_4 0.3 M, as supporting electrolyte), $[PdCl_2(PPh_3)_2]$ (16.8 mg, 0.03 mmol, 2 mM), and $EtN(iPr)_2$ (0.5 mL, 0.6 mmol). The rotating disk electrode was polarized at -1.2 V vs. SCE, on the plateau of the reduction current of $[PdCl_2(PPh_3)_2]$. The decreasing reduction current was recorded versus time after the addition of H₂O (1 mL, 55 mmol), up to 100% conversion (Figure 2, a).

Supporting Information (see footnote on the first page of this article): Experimental details and kinetic curves.

Acknowledgments

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- [9] A diminution of about 13% in the reduction current (not shown in Figure 2, a) was observed just after the addition of water (within less than 5 s) because of the dilution induced by the addition of water (1 mL, ca. 9%). Part of the current decrease was also due to the partial formation of complex 4 (not reduced at -1.2 V) in a fast reaction controlled by the concentration of hydroxide (see text).
- [10] The kinetic law that takes into account the fact that the kinetics was not investigated under pseudo-first-order conditions for Cl⁻ and HO⁻ was determined: $\ln x 3.3 \ln(2.3 + x) + 4 = -1.15 k_{re} K_{Cl} t$. $K_{Cl} k_{re} = 2.6 \times 10^{-3} \text{ s}^{-1}$ was calculated from the plot of $\ln x 3.3 \ln(2.3 + x) + 4$ vs. time (Figure S7).
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