

Evidence for an Equilibrium between Neutral and Cationic Arylpalladium(II) Complexes in DMF. Mechanism of the Reduction of Cationic Arylpalladium(II) Complexes

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Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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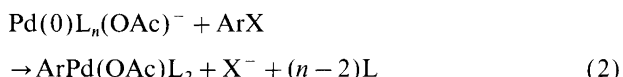
In DMF, neutral arylpalladium(II) complexes $\text{ArPdX}(\text{PPh}_3)_2$ ($\text{Ar} = \text{Ph}$; $\text{X} = \text{Cl}$, Br , I , OAc) are involved in an equilibrium with the cationic complex $\text{ArPd}(\text{PPh}_3)_2(\text{DMF})^+$ and the anion X^- . The values of the equilibrium constants K_X have been determined and the affinity of X^- for $\text{ArPd}(\text{PPh}_3)_2(\text{DMF})^+$ is found to be in the order: $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{AcO}^-$. Therefore, albeit the usual reactions with nucleophiles are performed from the neutral complex, the real reactive intermediate might well be the cationic complex. The electrochemical reduction of cationic complexes $\text{ArPd}(\text{PPh}_3)_2^+$ affords biaryl, and the mechanism of this reaction has been investigated. It proceeds via transient arylpalladium(I) complexes.

Neutral σ -arylpalladium(II) complexes, ArPdXL_2 ($\text{L} =$ phosphine, $\text{X} = \text{Cl}$, Br , I) are postulated to be key intermediates in palladium-catalyzed reactions involving aryl halides¹⁻⁸ (cross-coupling reactions, Heck reactions, carbonylation). They all result from the oxidative addition of a neutral palladium(0) complex to an aryl halide:



with $\text{L} = \text{L}' =$ phosphine⁹⁻¹¹ or $\text{L} =$ phosphine and $\text{L}' =$ dba (dibenzylideneacetone).¹²⁻¹⁴

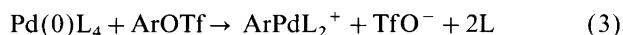
It has also been established that $\text{ArPd}(\text{OAc})\text{L}_2$ complexes are key intermediates in Heck reactions.¹⁵ Indeed, under these conditions [i.e. $\text{Pd}(\text{OAc})_2$ and $n\text{L}$ as precursor of palladium(0) complexes], $\text{ArPd}(\text{OAc})\text{L}_2$ complexes are generated from the oxidative addition of an aryl halide to an anionic palladium(0) complex, ligated by one acetate ion.¹⁵⁻¹⁷



$\text{ArPd}(\text{OAc})\text{L}_2$ complexes are also involved in the palladium-catalyzed Miyaura-Suzuki reactions when performed in the presence of acetate anions.¹⁸

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On the other hand, cationic σ -arylpalladium(II) complexes, ArPdL_2^+ have been characterized in oxidative additions performed from aryl triflates.¹⁹



Therefore, depending on the aryl derivative and the palladium(0) complex active in the oxidative addition, neutral complexes ArPdXL_2 ($\text{X} = \text{Cl}$, Br , I , OAc) or cationic complexes ArPdL_2^+ are formed in oxidative additions and may thus be involved in further steps of a catalytic cycle. All these arylpalladium(II) complexes have been characterized by electrochemical techniques,^{15,20} spectroscopy (³¹P NMR^{12,15,18,20} and ¹H NMR^{15,19,20}), conductimetry¹⁹ and their reactivity can be monitored by means of electrochemical techniques. In our attempt to characterize such complexes by cyclic voltammetry, we have observed that whereas ArPdXL_2 ($\text{L} = \text{PPh}_3$; $\text{X} = \text{Br}$, I) complexes were reduced in a single reduction peak in THF,²⁰ two distinct reduction peaks were detected when the reduction was performed in DMF. This suggests that in a coordinating solvent such as DMF, the neutral complexes could be involved in an equilibrium with the cationic complex, $\text{ArPdL}_2(\text{DMF})^+$. If so, the apparent reactivity of neutral complexes in

nucleophilic attacks for example, might be due in fact to cationic complexes. In the context of our constant search for the identification of the real reactive intermediates in usual catalytic cycles,^{12,15,20} we wish to report a new evidence for the existence of an equilibrium between neutral and cationic arylpalladium(II) complexes. Some electrochemical properties of cationic arylpalladium(II) complexes, ArPdL_2^+ have also been investigated and are reported thereafter.

Experimental

Chemicals. All experiments were performed under argon. DMF (Janssen) was distilled over calcium hydride under vacuum and stored under an argon atmosphere. $\text{PhPdX}(\text{PPh}_3)_2$ ($X=\text{I},^9 \text{Br},^{10} \text{Cl},^{11} \text{OAc}^{15,18}$) and $\text{PhPd}(\text{PPh}_3)_2^+, \text{BF}_4^-$ (Ref. 15) were synthesized according to published procedures.

Instrumentation. Cyclic voltammetry was performed with a home made potentiostat and a waveform generator (Tacussel GSTP4). The cyclic voltammograms were recorded on a Nicolet oscilloscope.

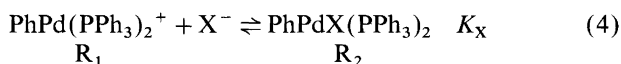
Electrochemical experiments. Experiments were performed in a three-electrode cell connected to a Schlenk line. The working electrodes consisted of a gold disk of 0.5 or 0.125 mm diameter. The counter-electrode was a platinum wire of ca. 1 cm² apparent surface area. The reference was a saturated calomel electrode separated from the solution by a bridge filled with a solution of *n*-Bu₄NBF₄ (0.3 mol dm⁻³) in 3 mL of DMF. A 12 mL volume of DMF containing the same concentration of supporting electrolyte was poured into the cell. A 0.024 mmol (2 mmol dm⁻³) amount of $\text{PhPdX}(\text{PPh}_3)_2$ ($X=\text{I}, \text{Br}, \text{Cl}, \text{OAc}$) or $\text{PhPd}(\text{PPh}_3)_2^+, \text{BF}_4^-$ was then added and cyclic voltammetry was performed at different scan rates, from 0.05 to 500 V s⁻¹. Simple step chronoamperometry was performed in the same cell, with the same equipment, in the range of potentials from -1 to -2.3 V, on 0.024 mmol (2 mmol dm⁻³) of $\text{PhPdX}(\text{PPh}_3)_2$ ($X=\text{I}, \text{Br}, \text{OAc}$), for step duration times θ from 20 to 200 ms.

Results and discussion

Evidence for an equilibrium between neutral ArPdXL_2 ($X=\text{Cl}, \text{Br}, \text{I}, \text{OAc}$) and cationic ArPdL_2^+ complexes. Neutral $\text{PhPdX}(\text{PPh}_3)_2$ ($X=\text{Cl}^{15}, \text{Br},^{15} \text{I},^{12,15} \text{OAc}^{15,18}$) and cationic $\text{PhPd}(\text{PPh}_3)_2^+, \text{BF}_4^-$ (Ref. 15) complexes have already been characterized by ³¹P NMR spectroscopy in THF and DMF, as singlet signals. This shows that the two phosphorus atoms are equivalent in the neutral and cationic complexes, confirming a *trans* square planar structure for the neutral complexes, as already established¹⁰ and also seen for the cationic complex¹⁹ with the solvent *S* as the fourth ligand $\text{PhPd}(\text{PPh}_3)_2(\text{S})^+, \text{BF}_4^-$ (the solvent *S* will be omitted

in the following for simplification). On the other hand, the presence of a unique signal for the neutral complexes which differs from the signal of the cationic complex establishes that, in both solvents, the neutral complexes are present in solution as the major form, or that there is a full dynamic equilibrium between the neutral and cationic complexes, within the timescale (ca. 1 s) of ³¹P NMR spectroscopy, performed at 162 MHz.

As already reported,²⁰ the electrochemical reduction of neutral complexes $\text{PhPdX}(\text{PPh}_3)_2$ ($X=\text{Cl}, \text{Br}, \text{I}$) (2 mmol dm⁻³) performed in THF (containing *n*-Bu₄NBF₄, 0.3 mmol dm⁻³), involved a single bielectronic reduction peak, whatever the scan rate. But surprisingly, when the reduction of the same neutral complexes $\text{PhPdX}(\text{PPh}_3)_2$ ($X=\text{Br}, \text{I}, \text{OAc}$) was performed in DMF (containing *n*-Bu₄NBF₄, 0.3 mmol dm⁻³) at a scan rate of 0.20 V s⁻¹, two reduction peaks R₁ and R₂ were observed, as shown in Table 1 and illustrated in Fig. 1a for $\text{PhPdBr}(\text{PPh}_3)_2$ and in Fig. 3 of Ref. 15 for $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$. This means either that the mechanism of the reduction of the neutral arylpalladium(II) complex is more complex in DMF than in THF and proceeds in two steps, or that two different complexes are present in DMF solution. When either bromide anions (introduced as *n*-Bu₄NBr) were added to a solution of $\text{PhPdBr}(\text{PPh}_3)_2$ in DMF, or acetate anions (introduced as *n*-Bu₄NOAc) to a solution of $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$, one observed an increase of the reduction peak current of R₂ at the expense of that of R₁. When a large excess of bromide ions was added to $\text{PhPdBr}(\text{PPh}_3)_2$, only reduction peak R₂ was observed (Fig. 1c). This demonstrates that the free anion X⁻ is involved in an equilibrium with the neutral arylpalladium(II) complex which is reduced at R₂, and consequently with the cationic arylpalladium(II) complex which is reduced at R₁ [eqn. (4)].



Thus, the cationic complex is observed by cyclic voltammetry in DMF solutions containing the neutral complexes, although its ³¹P NMR signal cannot be detected (see above). This arises from the fact that the cationic complex is reduced at R₁ (at a less reductive potential

Table 1. Reduction potentials of $\text{PhPdX}(\text{PPh}_3)_2$ (2 mmol dm⁻³) in DMF.

$\text{PhPdX}(\text{PPh}_3)_2$ X	R ₁ $E^{\text{R}_1}/\text{V vs. SCE}^a$	R ₂ $E^{\text{R}_2}/\text{V vs. SCE}^a$
Cl	— ^b	-1.99
Br	-1.75	-1.95
I	-1.65	-1.95
OAc	-1.83	-2.03

^aThe reduction potentials were determined in DMF containing *n*-Bu₄NBF₄ (0.3 mol dm⁻³) at a gold disk electrode (i.d.=0.5 mm) with a scan rate of 0.2 V s⁻¹. 20 °C. ^bNot observed.

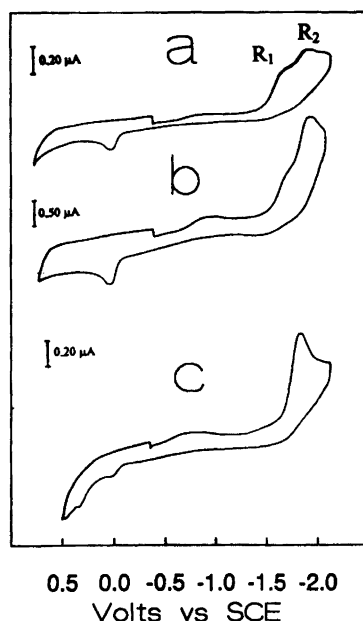


Fig. 1. Cyclic voltammetry of $\text{PhPdBr}(\text{PPh}_3)_2$ (2 mmol dm^{-3}) in DMF (containing $n\text{-Bu}_4\text{NBF}_4$, 0.3 mol dm^{-3}) at a stationary gold disk electrode (i.d. = 0.5 mm) at 20°C . (a) With a scan rate of 0.2 V s^{-1} . (b) With a scan rate of 2 V s^{-1} . (c) In the presence of 10 equiv. of $n\text{-Bu}_4\text{NBr}$, with a scan rate of 0.2 V s^{-1} .

than R_2) and that its reduction at the electrode surface causes a continuous shift of the equilibrium (4) to its left-hand side. Under these conditions, the concentration of the cationic complex, measured by its reduction peak current, is not its real concentration in the solution but reflects a dynamic concentration²¹ due to a shift of the equilibrium (4), when the electrochemical reduction is performed. Evidence for the equilibrium (4) is also confirmed by the relative variation of the reduction peak currents, i_{R_1} and i_{R_2} , when the scan rate was varied (Fig. 1b), a phenomenon that characterizes a CE mechanism.²¹ When the cyclic voltammetry was performed on a solution of $\text{PhPdCl}(\text{PPh}_3)_2$ (2 mmol dm^{-3} in DMF), the reduction peak of the cationic complex at R_1 was not observed (Table 1) even at a lower scan rate (0.05 V s^{-1}). This shows that in DMF, the equilibrium (4) is more in favor of the neutral complex $\text{PhPdCl}(\text{PPh}_3)_2$, compared to the other complexes where $X = \text{Br}$, I or OAc and/or that the rate constant of the formation of the cationic complex is smaller.

Before investigating the thermodynamics of the equilibrium (4) between neutral and cationic phenylpalladium(II) complexes, by comparing their respective reduction peak currents at R_1 and R_2 , it was necessary to determine the number of electrons involved in the electrochemical reduction of the cationic complex $\text{PhPd}(\text{PPh}_3)_2^+$ at R_1 . It is already established that the reduction of neutral complexes, $\text{PhPdX}(\text{PPh}_3)_2$ ($X = \text{I}$, Br , Cl), when alone in solution as in THF,²⁰ involves two electrons at R_2 . When cyclic voltammetry was performed on a solution of an authentic sample of the

cationic complex $\text{PhPd}(\text{PPh}_3)_2^+ \cdot \text{BF}_4^-$ (2 mmol dm^{-3} in DMF), an irreversible reduction peak R_3 was observed at -1.83 V (Fig 2a). The reduction peak potential of the cationic complex alone in solution is very similar to those observed for wave R_1 , ascribed to the cationic complex when the latter is involved in an equilibrium with the neutral complexes (Table 1). The reduction potentials determined at R_1 , although attributed to the same species, i.e. the cationic complex, could not have the same value, whatever X. Indeed, we are considering peak potentials and not standard potentials. The reduction of the cationic complex obeys a CEC mechanism, and the value of its reduction peak potential depends in particular on the value of the equilibrium constant K_X and on the dynamics of the corresponding equilibrium. Moreover, owing to the proximity of peaks R_1 and R_2 , the potential of wave R_1 could not be precisely determined. The reduction peak R_3 of $\text{PhPd}(\text{PPh}_3)_2^+ \cdot \text{BF}_4^-$, became reversible at high scan rates (Fig. 2c), and the plot of its reduction peak current i_{R_3} versus the square root of the

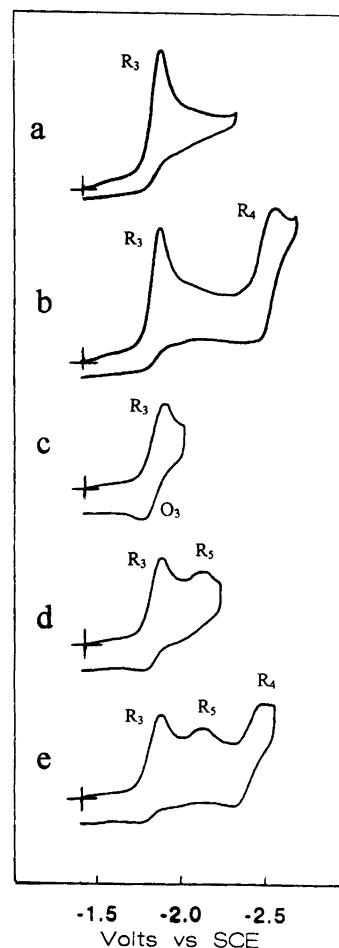
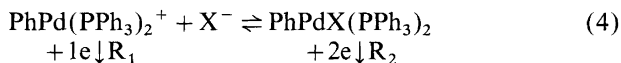


Fig. 2. Cyclic voltammetry of $\text{PhPd}(\text{PPh}_3)_2^+ \cdot \text{BF}_4^-$ (2 mmol dm^{-3}) in DMF (containing $n\text{-Bu}_4\text{NBF}_4$, 0.3 mol dm^{-3}) at 20°C . (a) and (b) At a stationary gold disk electrode (i.d. = 0.5 mm), with a scan rate of 0.2 V s^{-1} . (c)–(e) At a stationary gold disk electrode (i.d. = 0.125 mm), with a scan rate of 500 V s^{-1} .

scan rate was found to be linear (Fig. 3). This demonstrates that the number of electrons involved in the electrochemical reduction of the cationic complex at R_3 was constant whatever the scan rate, i.e. it did not change in the timescale investigated here. Determination of the absolute number of electrons²² involved at long times ($\theta=200$ ms) showed that $n=1.2 \pm 0.1$. Therefore, the reduction of the cationic complex $\text{PhPd}(\text{PPh}_3)_2^+$ at R_1 is a monoelectronic process, whereas the reduction of the neutral complexes $\text{PhPdX}(\text{PPh}_3)_2$ ($X=\text{Cl}, \text{Br}, \text{I}$) at R_2 is bielectronic,²⁰ whatever the timescale.



$$K_X = \frac{[\text{PhPdX}(\text{PPh}_3)_2]}{[\text{PhPd}(\text{PPh}_3)_2^+][\text{X}^-]}$$

The equilibrium constant K_X was determined by chronoamperometry.²³ In Fig. 4 are shown two plots of $i\theta^{1/2}$ as a function of the pulse potential, for different step duration times θ .²³ These two plots indicate that the reduction current of R_1 decreases relatively to that of R_2 when θ decreases, as in a CE mechanism.²¹ The ratio $i_{R_1}/(i_{R_1} + i_{R_2}/2)$, where i is the diffusion current determined on the respective plateau of R_1 and R_2 , is plotted as a function of $\log \theta$ in Fig. 5. A plateau was observed at short times, and the equilibrium constant K_X was calculated from the value of this plateau. The equilibrium constants K_X are reported in Table 2 for $X=\text{Br}, \text{I}$ and OAc . K_{Cl} could not be of course calculated with this technique because the cationic complex was not detected in a solution of $\text{PhPdCl}(\text{PPh}_3)_2$ in DMF, even at long times (see above). K_{Cl} was deduced from the equilibrium constant K of the equilibrium (5) already determined in

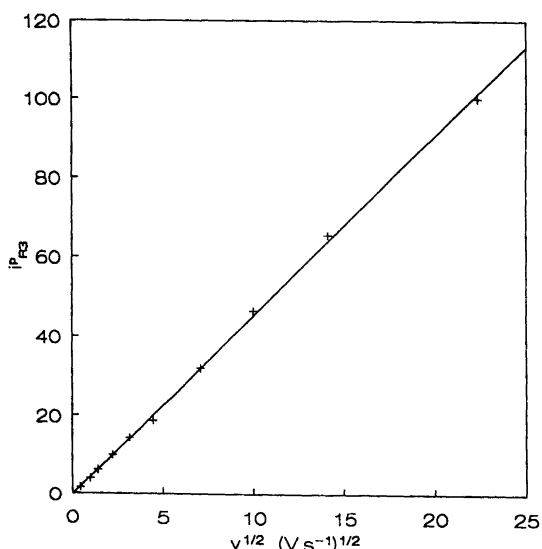


Fig. 3. Variation of the reduction peak current $i_{R_3}^p$ of $\text{PhPd}(\text{PPh}_3)_2^+, \text{BF}_4^-$ (2 mmol dm^{-3}) in DMF (containing $n\text{-Bu}_4\text{NBF}_4$, 0.3 mol dm^{-3}) as a function of the square root of the scan rate, at 20°C . Gold disk electrodes (i.d.=0.5 and 0.125 mm). Arbitrary units for $i_{R_3}^p$. $r=0.9995$.

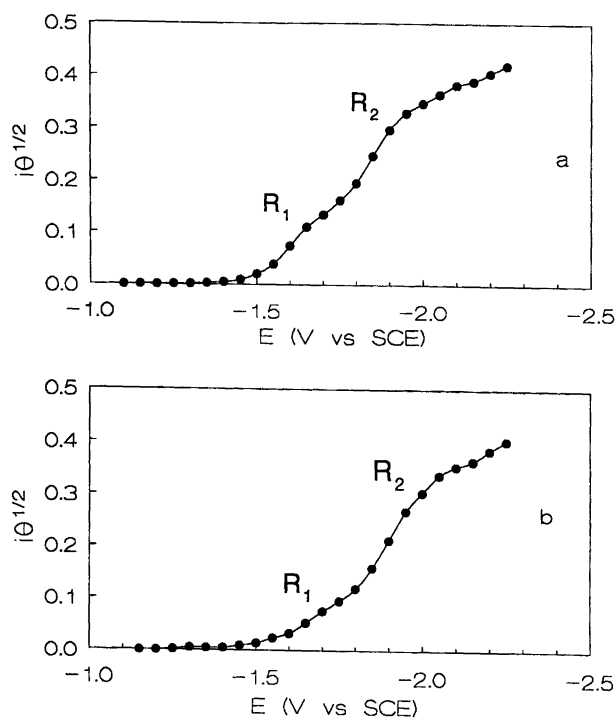


Fig. 4. Chronoamperometric reduction of $\text{PhPdBr}(\text{PPh}_3)_2$ (2 mmol dm^{-3}) in DMF (containing $n\text{-Bu}_4\text{NBF}_4$, 0.3 mol dm^{-3}) at 20°C . Variation of $i\theta^{1/2}$ as a function of the pulse potential for different step duration times θ . (a) $\theta=200$ ms, at a gold disk electrode (i.d.=0.5 mm). (b) $\theta=20$ ms, at a gold disk electrode (i.d.=0.125 mm).

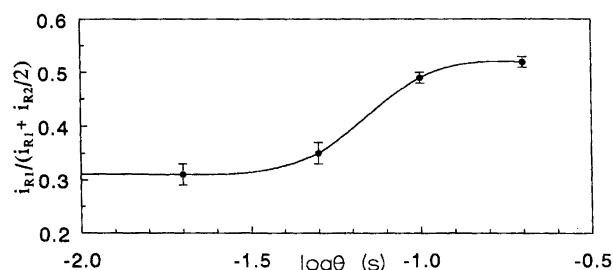
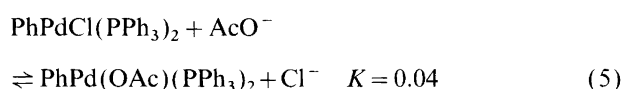


Fig. 5. Variation of the ratio $i_{R_1}/(i_{R_1} + i_{R_2}/2)$ [i , diffusion current determined on the respective plateau of R_1 and R_2 (Fig. 4) for the reduction of $\text{PhPdBr}(\text{PPh}_3)_2$ (2 mmol dm^{-3}) in DMF containing $n\text{-Bu}_4\text{NBF}_4$, 0.3 mol dm^{-3}] as a function of the step duration time θ . 20°C .

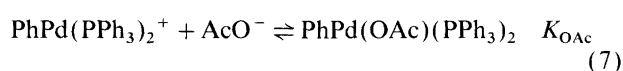
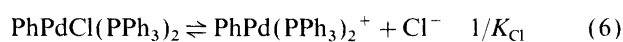
Table 2. Determination of the equilibrium constant K_X in DMF at 20°C :

$\text{PhPd}(\text{PPh}_3)_2^+ + \text{X}^- \rightleftharpoons \text{PhPdX}(\text{PPh}_3)_2$	K_X
X	$K_X/\text{mol}^{-1} \text{ dm}^3$
Cl	19×10^3
Br	3.6×10^3
I	1.7×10^3
OAc	0.75×10^3

DMF, in a previous work.¹⁵



Indeed, this equilibrium may be related to the cationic complex, according to the following sequence involving two successive equilibria:

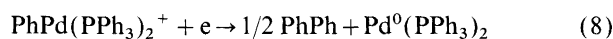


from which one calculates the value of $K_{\text{Cl}} = K_{\text{OAc}}/K$. From the values of K_{X} collected in Table 2, one deduces that, in DMF, the affinity of the anion X^- for $\text{PhPd}(\text{PPh}_3)_2(\text{DMF})^+$ follows the expected decreasing order: $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{AcO}^-$.

Thus, it is established that, in DMF, neutral complexes ArPdXL_2 ($\text{L} = \text{PPh}_3$, $\text{X} = \text{Cl}$, Br , I , OAc) are involved in an equilibrium with the cationic complex, $\text{ArPdL}_2(\text{DMF})^+$. The contribution of the cationic complex is more important for OAc^- than for Cl^- . Therefore, one has to be extremely careful before claiming that a neutral arylpalladium(II) complex is the key intermediate in a given reaction because it was found to be reactive in this reaction. Indeed, the reaction may well proceed via the cationic complex in equilibrium with the neutral complex.

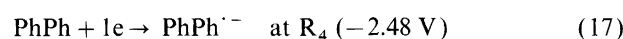
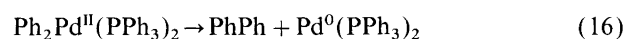
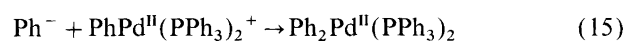
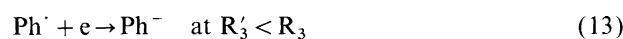
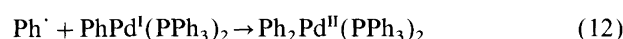
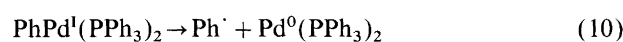
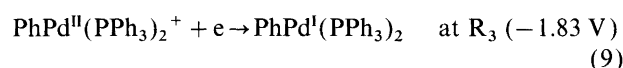
To decide on the nature of the real reactive species, one has first to check whether the cationic arylpalladium(II) complex reacts under the same conditions employed for the neutral complex and establish which reaction is faster. We had to face this problem in our search for the intermediate in Heck reactions.¹⁵ Indeed, after $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$ had been identified as the complex resulting from the oxidative addition [eqn. (2)],¹⁵⁻¹⁷ it was found to react with styrene to afford stilbene, according to the classical Heck reaction.¹⁵ Since we had already gained evidence for the existence of equilibrium (7),^{15,24} we have investigated the reactivity of the isolated cationic complex $\text{PhPd}(\text{PPh}_3)_2^+, \text{BF}_4^-$ with styrene under the same experimental conditions as for $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$. These experiments showed that the cationic complex did react with the styrene but the reaction was slower than that with $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$, demonstrating that the latter complex and not the cationic complex, was the real intermediate in the Heck reaction.¹⁵ But had the reaction with the isolated cationic complex been faster than that with $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$, the conclusion could have been the reverse one. This shows that the complex which is thought to react, might be or not be the real intermediate, as soon as both are involved in a rapid equilibrium. In this respect, it is worth to recall here that it has recently been reported that some cationic organopalladium(II) complexes were more reactive than the corresponding neutral organopalladium(II) halides complexes.^{25-29,34,35}

Mechanism of the reduction of cationic ArPdL_2^+ complexes. When the reductive voltammetry of $\text{PhPd}(\text{PPh}_3)_2^+, \text{BF}_4^-$ (2 mmol dm^{-3}) in DMF at 0.2 V s^{-1} , was pursued beyond the reduction peak R_3 , a second reduction peak R_4 was detected at $E_{\text{R}_4} = -2.48 \text{ V}$ and assigned to the reduction of biphenyl by comparison with an authentic sample (Fig. 2b). An exhaustive electrolysis was performed on a solution of $\text{PhPd}(\text{PPh}_3)_2^+, \text{BF}_4^-$ (2 mmol dm^{-3} in DMF containing $n\text{-Bu}_4\text{NBF}_4$, 0.3 mol dm^{-3}) at a controlled potential of -1.8 V . The composition of the solution was monitored by cyclic voltammetry, as a function of the charge passed through the cell. After consumption of 1 F mol^{-1} , the cyclic voltammogram exhibited only the reduction peak R_4 of biphenyl and an oxidation peak at 0 V , characteristic of a palladium(0) complex ligated by PPh_3 . Biphenyl was analyzed by HPLC and shown to be produced in quantitative yield.



At shorter times, when the scan rate was increased up to 500 V s^{-1} , (Figs. 2c-2e), the first reduction peak R_3 became progressively reversible, a third reduction peak R_5 was growing concomitantly at -2.16 V , while the reduction peak current of the biphenyl at R_4 decreased when compared to that of R_3 (cf. Figs. 2b and 2e). Increasing the scan rate, i.e. decreasing the timescale, thus resulted in a lower production of biphenyl while a transient short-lived intermediate palladium complex was detected at R_5 .

Since the reduction of $\text{PhPd}(\text{PPh}_3)_2^+, \text{BF}_4^-$ at R_3 was found to involve one electron whatever the timescale (see above), it means that at long times, the monoelectronic reduction of $\text{PhPd}(\text{PPh}_3)_2^+, \text{BF}_4^-$ affords biphenyl probably through the sequence of Scheme 1.

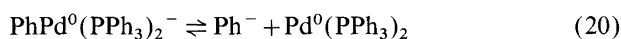
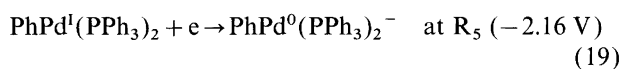
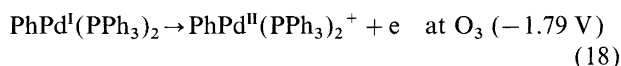
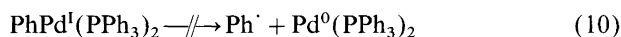
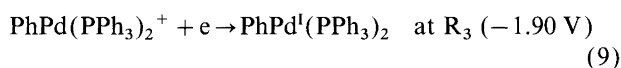


Scheme 1. Mechanism of the reduction of $\text{PhPd}(\text{PPh}_3)_2^+$ at long times.

The first electron transfer affords a phenylpalladium(I) complex $\text{PhPd}^{\text{I}}(\text{PPh}_3)_2$ which dissociates to palladium(0) and a phenyl radical Ph^\cdot [eqn. (10)] with a rate constant of ca. $(2-3) \times 10^3 \text{ s}^{-1}$. This radical cannot dimerize to biphenyl because it is produced at a potential where it is

reducible.³⁶ Since on the other hand, no significant benzene formation was observed in electrolysis, but exclusively PhPh, we are forced to consider that the radical Ph[•] ends up into the exclusive formation of Ph₂Pd^{II}(PPh₃)₂, this latter species yielding eventually PhPh {detected by its reduction peak at R₄ [eqn. (17)]} after a reductive elimination [eqn. (16)]. Two alternative sequences are possible *a priori* for the formation of Ph₂Pd^{II}(PPh₃)₂ from the radical Ph[•] and they cannot be distinguished on the basis of the present experiments. Both are reported in Scheme 1. A first possibility amounts to consider a direct attack of PhPd^I(PPh₃)₂ by Ph[•] [eqn. (12)]. The second possibility consists in a reduction of the phenyl radical (at the electrode or homogeneously) to the phenyl anion, which then reacts with the cationic complex [eqn. (15)]. In practice, since the cleavage of PhPd^I(PPh₃)₂ is not so fast, reduction of Ph[•] (if occurring) has to be homogeneous,³⁷ through electron transfer with PhPd^I(PPh₃)₂. So kinetically the above distinction is rather subtle, since it amounts to deciding between direct radical coupling [Ph[•] and PhPd^I(PPh₃)₂] or electron transfer followed by anion coupling [Ph⁻ and PhPd^{II}(PPh₃)₂].³⁸

At shorter times (Figs. 2c–2e), the reduction of PhPd(PPh₃)₂⁺ became partially reversible, indicating that reaction (10), in which a phenyl radical dissociated from the palladium atom was partially frozen, and consequently the reduction of the phenylpalladium(I), PhPd^I(PPh₃)₂ generated by reduction of the PhPd(PPh₃)₂⁺, could be observed at R₅ [ca. 65% of PhPd^I(PPh₃)₂ has dissociated according to eqn. (10) within 0.5 ms, Fig. 2d]. The mechanism of the reduction of the cationic complex at short times is summarized in Scheme 2.



Scheme 2. Mechanism of the reduction of PhPd(PPh₃)₂⁺ at short times.

If the time is not short enough, reaction (10) could be partially operating and some biphenyl will be produced by reactions (12), (15) and (16) of Scheme 1. This is observed in Fig. 2e, where the reduction peak of PhPd^I(PPh₃)₂ at R₅ is not fully developed (its reduction peak current is less than that of R₃). The anionic phenylpalladium(0) complex PhPd⁰(PPh₃)₂⁻, generated by reduction of PhPd^I(PPh₃)₂ in eqn. (19), dissociates to palladium(0) and phenyl anion Ph⁻, as already established²⁰ [eqn. (20)]. We cannot exclude that, even at this

timescale ($v=500 \text{ V s}^{-1}$), Ph⁻ could react with PhPd(PPh₃)₂⁺ to produce biphenyl, as proposed in Scheme 1 [eqns. (15) and (16)].³⁹

Therefore, the mechanism of the reduction of the cationic complex PhPd(PPh₃)₂⁺, which affords biphenyl, is a complex process which proceeds through a transient phenylpalladium(I) complex, PhPd^I(PPh₃)₂. This phenylpalladium(I) complex has until now never been observed because of its decomposition to phenyl radical and palladium(0) or because it is usually produced at a potential where it is reducible. Indeed, it is also probably generated by reduction of neutral phenylpalladium(II) complexes, PhPdX(PPh₃)₂, but this reduction occurs at around -2 V, i.e. at a potential where the phenylpalladium(I) is already reduced and the overall reduction involves 2 electrons per mole, leading to the formation of benzene.²⁰ The cationic complex is more easily reduced (-1.83 V) than the neutral complexes. The phenylpalladium(I), PhPd^I(PPh₃)₂, can thus be generated by reduction of the cationic complex at a potential where PhPd^I(PPh₃)₂ is not reduced and therefore the latter complex can be detected at short times, i.e. before its dissociation. This contrasts with arylpalladium(II) complexes ligated by bidentate phosphine ligand such as PhPdI(dppe), whose reduction in THF at -1.79 V involves one electron.²⁰ It seems that in the case of dppe, PhPd^I(dppe) does not dissociate, and moreover is generated at a potential where it is not reduced. The same observation was made for PhNi^I(dppe) complex, which was found to be a key intermediate in nickel-catalyzed dimerization of phenyl halides.⁴⁰

Conclusion

In DMF, neutral arylpalladium(II) complexes ArPdX(PPh₃)₂ (X=Cl, Br, I, OAc) are involved in an equilibrium with the cationic complex ArPd(PPh₃)₂(DMF)⁺ and the anion X⁻. The affinity of X⁻ for the cationic complex follows the order: Cl⁻ > Br⁻ > I⁻ > AcO⁻. Therefore, reactions of neutral arylpalladium(II) complexes might proceed via cationic complexes ArPd(PPh₃)₂(DMF)⁺ which thus might be the real intermediates in some palladium-catalyzed reactions.

The electrochemical reduction of the cationic phenylpalladium(II) complex PhPd(PPh₃)₂⁺ quantitatively affords biphenyl. A mechanism for this reaction is proposed, which involves transient short-lived phenylpalladium(I) complexes.

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24. In the ^{31}P NMR spectrum of $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$ generated under the Heck conditions, i.e. from the oxidative addition of PhI with the palladium(0) generated *in situ* in mixtures of $\text{Pd}(\text{OAc})_2$ and n PPh_3 ($n \geq 3$) as in eqn. (2),¹⁷ one observed, in both THF and DMF, the ^{31}P NMR signal of $\text{PhPd}(\text{PPh}_3)_2^+$ at 21.70 ppm together with that of $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$ at 21.25 ppm [see Fig. 2 in Ref. (15)], although the signal of the cationic complex is not detected in a solution of an authentic sample of $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$. This arises from the presence of protons which are generated when the palladium(0) complex is formed from $\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2$.¹⁷ In the presence of protons which react with the acetate anion, the equilibrium (7) is shifted to its left-hand side, to the formation of the cationic complex which is thus observed in ^{31}P NMR spectroscopy in appreciable amount. When the oxidative addition was performed in the presence of NEt_3 as a base, the amount of the cationic complex was less because protons have been partially neutralized.
25. As an example $\text{MePd}(\text{PMe}_3)_2^+$ was found to be 100 times more reactive with CO than the neutral complex $\text{MePdCl}(\text{PMe}_3)_2$. See: Kayaki, Y., Shimizu, I. and Yamamoto, A. *Chem. Lett.* (1995) 1089 and Ref. 26.
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27. It is the case for Heck reactions when they are performed from aryl halides in the absence of any acetate or halide anions. Indeed we have shown that the neutral $\text{PdPdI}(\text{PPh}_3)_2$ did not react with styrene whereas the cationic complex $\text{PdPd}(\text{PPh}_3)_2^+ \cdot \text{BF}_4^-$ did and afforded stilbene.¹⁵ See other examples reported by Yamamoto²⁸ and Brown,²⁹ such as papers in which the cationic complex is postulated to be the real intermediate in Heck reactions performed from aryl halides.^{30–33}
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39. When the cyclic voltammetry was performed at 500 V s^{-1} , as in Figs. 2c–2e, on solutions of the cationic complex at the concentration of 1 and 2 mM, one observed that in the more concentrated solution, the reduction peak of $\text{PhPd}^+(\text{PPh}_3)_2$ at R_5 increased relatively to that of $\text{PhPd}(\text{PPh}_3)_2^+$ at R_3 and that the amount of biphenyl detected at R_4 was smaller. This suggests that reaction (10) is an equilibrium which could be shifted to its left-hand side, i.e. to the formation of $\text{PhPd}^+(\text{PPh}_3)_2$, when the initial concentration of $\text{PhPd}(\text{PPh}_3)_2^+$ is increased, because the backward reaction of eqn. (10) is of second order. Increasing the concentration of the initial cationic complex also results in a shift of the equilibrium (20) to its left-hand side with, as consequences, a smaller production of biphenyl, as observed.
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