# Formation of Anionic PdX<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup> Complexes by Reaction of Halide Ions with PdX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>

Christian Amatore,\*<sup>[a]</sup> Anny Jutand,<sup>\*[a]</sup> and Loïc Mottier<sup>[a]</sup>

Keywords: Palladium / Anionic complexes / Phosphane substitution

Halide ions react with  $PdX_2(PPh_3)_2$  (X = Cl, Br, I) complexes in an equilibrated reaction in which the phosphane ligand is substituted by the halide X<sup>-</sup> to form anionic complexes  $PdX_3(PPh_3)^-$  in THF and DMF. The equilibrium constants have been determined by cyclic voltammetry.

#### Introduction

It has been established that halide ions are good ligands for palladium(0) complexes.<sup>[1-3]</sup> The best way to investigate the effect of halide ions on the structure and reactivity of palladium(0) complexes in oxidative addition with aryl halides<sup>[2-5]</sup> was to generate them by electrochemical reduction of  $PdX_2(PPh_3)_2$  in the presence of various amounts of halides  $X^{-}$  (X = Cl,<sup>[2][3]</sup> Br,<sup>[3]</sup> I<sup>[3]</sup>) in THF. However, during the course of these reactions, it was observed that the reduction peak of PdX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was affected by the presence of added X<sup>-</sup> so that its usual single bielectronic reduction peak became split into two peaks whose relative currents depended on the halide concentration: the higher the concentration of X<sup>-</sup>, the higher the second reduction peak current relative to the first one.<sup>[2][3]</sup> This phenomenon was first discarded and tentatively interpreted as the formation of an intermediate palladium(I) complex by reduction of the palladium(II) complex. Its stabilization by halide ions as an anionic 18-electron dimer e.g. [PdI(PPh<sub>3</sub>)<sub>2</sub>X<sub>2</sub>]<sub>2</sub><sup>2-</sup> would indeed make it less easily reduced than Pd<sup>II</sup>X<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, thus giving rise to the second reduction peak.<sup>[2][3]</sup>

However, careful investigation of this reaction led us now to reconsider our first tentative hypothesis and to establish that reactions of halides  $X^-$  with  $PdX_2(PPh_3)_2$  result in substitution of one phosphane ligand with formation of an anionic  $PdX_3(PPh_3)^-$  species; this palladium(II) complex is more difficult to reduce. In other words, the two peaks represent the reduction of two different palladium(II) complexes.<sup>[6]</sup>

### **Results and Discussion**

# Evidence of the Formation of $PdX_3(PPh_3)^-$ Complexes by Reaction of X<sup>-</sup> and $PdX_2(PPh_3)_2$ by <sup>31</sup>P-NMR Spectroscopy in THF and DMF

The <sup>31</sup>P-NMR spectra of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (3 mmol dm<sup>-3</sup>) in THF exhibited a single signal at  $\delta = 23.80$ . Two new

signals appeared in the presence of 120 equivalents of  $nBu_4NCl$  (Figure 1): one signal at  $\delta = -5.27$  characteristic of the phosphane PPh<sub>3</sub> and a second one at  $\delta = 27.42$  assigned to the anionic species PdCl<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup> by comparison with an authentic sample of [PdCl<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup>,  $nBu_4N^+$ ].<sup>[7]</sup>



Figure 1. <sup>31</sup>P-NMR spectrum (162 MHz) of a solution of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (3 mmol·dm<sup>-3</sup>) and *n*Bu<sub>4</sub>NCl (360 mmol dm<sup>-3</sup>) in 3 mL of THF and 0.2 mL of [D<sub>6</sub>]acetone with H<sub>3</sub>PO<sub>4</sub> as an external reference

The signal of  $PdCl_2(PPh_3)_2$  was still present even in the presence of a large excess of chloride ions suggesting that  $Cl^-$  substituted one phosphane from  $PdCl_2(PPh_3)_2$  through an equilibrated reaction (Equation 1).

$$Pd^{II}Cl_{2}(PPh_{3})_{2} + Cl^{-} \Longrightarrow Pd^{II}Cl_{3}(PPh_{3})^{-} + PPh_{3}$$
(1)

The dynamic of this equilibrium is relatively slow compared to the time-scale of the NMR experiment since three distinct narrow signals were observed for  $PdCl_2(PPh_3)_2$ ,  $PdCl_3(PPh_3)^-$ , and  $PPh_3$  (Figure 1). Similar equilibria have been observed using <sup>31</sup>P-NMR spectroscopy by treating  $nBu_4NBr$  with  $PdBr_2(PPh_3)_2$  and  $nBu_4NI$  with  $PdI_2(PPh_3)_2$ in THF (Equation 2, Table 1).

$$Pd^{II}X_{2}(PPh_{3})_{2} + X^{-} \Longrightarrow Pd^{II}X_{3}(PPh_{3})^{-} + PPh_{3} \qquad K_{X} \qquad (2)$$

X = Cl, Br, I

In DMF, in the absence of any added halide ions, the  $^{31}P\text{-}NMR$  spectra of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> exhibited three signals. The major signal at  $\delta=24.4$  is assigned to PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The two other minor (10%) but of same magnitude signals are assigned to PPh<sub>3</sub> ( $\delta=-5.54$ ) and to the dimer

 <sup>[</sup>a] Ecole Normale Supérieure, Département de Chimie, CNRS URA 1679, 24 Rue Lhomond, F-75231 Paris Cedex 5, France Fax: (internat.) + 33-1/44323325 E-mail: Amatore@ens.fr Anny.Jutand@ens.fr

## **FULL PAPER**

x		Cl	Br	Ι	Cl	Br	Ι
$PdX_2(PPh_3)_2$ $PdX_2(PPh_3)_2$ $PdX_3(PPh_3)^-$ $PdX_3(PPh_3)^-$	THF DMF THF DMF	$\delta^{[a]}$ 23.80 24.36 27.42 28.12	$\delta^{[a]}$ 22.57 22.86 29.3	$ \begin{matrix} \delta^{[a]} \\ 13.34 \\ 13.35 \\ 30.70 \end{matrix} $	$\begin{array}{c} E^{\rm p}  [{\rm V}]^{\rm [b]} \\ -1.040 \\ -1.015 \\ -1.255 \\ -1.370 \end{array}$	$E^{\rm p} [V]^{\rm [b]} -0.830 -1.075$	$E^{\rm p} [V]^{\rm [b]} -0.725 -1.025$

Table 1. <sup>31</sup>P-NMR signals and reduction peak potentials of palladium(II) complexes involved in the equilibrium  $PdX_2(PPh_3)_2 + X^- \Rightarrow PdX_3(PPh_3)^- + PPh_3$ , with  $nBu_4N^+$  as the countercation

<sup>[a]</sup>162 MHz versus H<sub>3</sub>PO<sub>4</sub> as external standard. - <sup>[b]</sup> Volt versus SCE at a gold disk electrode at 0.2 V s<sup>-1</sup> at 25 °C.

 $Pd_2Cl_4(PPh_3)_2$  ( $\delta = 33.54$ ) by comparison with authentic samples.<sup>[9]</sup> These results suggest that the equilibrium according to Equation 3<sup>[10]</sup> operates in DMF and not in THF and is frozen on the time-scale of <sup>31</sup>P-NMR spectroscopy.

$$2 \operatorname{PdCl}_2(\operatorname{PPh}_3)_2 \longrightarrow \operatorname{Pd}_2\operatorname{Cl}_4(\operatorname{PPh}_3)_2 + 2 \operatorname{PPh}_3$$
(3)

In DMF, the <sup>31</sup>P-NMR spectra of PdBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> also exhibited three signals. However, the signal at  $\delta = 25.47$ , assigned to the dimer Pd<sub>2</sub>Br<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>, was detected at traces level compared to that of PdBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> at  $\delta = 22.86$ . A solution of PdI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> exhibited a single signal at  $\delta = 13.40$  in DMF suggesting that the dimer Pd<sub>2</sub>I<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> was not formed.

# Determination of the Equilibrium Constant $K_X$ by Cyclic Voltammetry in THF and DMF

As recalled in the introduction, progressive addition of  $nBu_4NCl$  to a solution of  $PdCl_2(PPh_3)_2$  (1.5 mmol·dm<sup>-3</sup> in THF containing  $nBu_4NBF_4$  0.3 mol·dm<sup>-3</sup>) provoked a split of its bielectronic reduction peak  $R_1$  at  $E^p = -1.04$  V versus SCE into two reduction peaks,  $R_1$  and  $R_2$  at  $E^p = -1.25$  V versus SCE (Figure 2a).<sup>[2][3]</sup>



Figure 2. Cyclic voltammetry performed in THF (containing  $nBu_4NBF_4$ , 0.3 mol·dm<sup>-3</sup>) at a steady gold disk electrode (i.d. = 0.5 mm) with a scan rate of 2 V s<sup>-1</sup>, at 25 °C: (a) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.5 mmol·dm<sup>-3</sup>) in the presence of 0 (—), 14 (– – –), 85 (…) equivalents of  $nBu_4NCl$ ; (b) [PdCl<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup>,  $nBu_4N^+$ ] (0.8 mmol·dm<sup>-3</sup>): alone (—); in the presence of 10 equivalents of PPh<sub>3</sub> (…)

From the <sup>31</sup>P-NMR investigation reported above, it can be inferred that the second reduction peak is not relevant to the reduction of intermediate palladium(I) complexes as earlier proposed<sup>[2][3]</sup> but to the reduction of the anionic divalent complex  $Pd^{II}Cl_3(PPh_3)^-$ . This assumption has been confirmed by the cyclic voltammetry of an authentic sample of  $[PdCl_3(PPh_3)^-$ ,  $nBu_4N^+]^{[7]}$  performed in THF which exhibited the unique reduction peak  $R_2$  (Figure 2b). Moreover, when 10 equivalents of PPh<sub>3</sub> were added to PdCl<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup>, the reduction peak  $R_2$  of PdCl<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup> disappeared and was replaced by the reduction peak  $R_1$  of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (Figure 2b), evidencing the backward reaction of equilibrium 2 (X = Cl).

$$\begin{array}{c} \operatorname{PdX}_{2}(\operatorname{PPh}_{3})_{2} + X^{*} \rightleftharpoons \operatorname{PdX}_{3}(\operatorname{PPh}_{3})^{*} + \operatorname{PPh}_{3} \\ R_{1} \\ \end{array}$$

$$\begin{array}{c} (2) \\ R_{2} \end{array}$$

The formation of anionic species was also observed by performing cyclic voltammetry on mixtures of  $nBu_4NBr$  and PdBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, as well as on mixtures of  $nBu_4NI$  and PdI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in THF. The reduction peak potentials of the neutral and anionic complexes are collected in Table 1.

From <sup>31</sup>P-NMR spectroscopy, the equilibrium according to Equation 2 was found to be slow compared to the timescale of the NMR experiment. In cyclic voltammetry, the reduction of  $PdX_2(PPh_3)_2$  at  $R_1$  is governed by a CE mechanism.<sup>[11]</sup> If the equilibrium according to Equation 2 is fast compared to the time-scale of the cyclic voltammetry, reduction of  $PdX_2(PPh_3)_2$  at  $R_1$  should result in a shift of the equilibrium to its left-hand side by the continuous consumption of  $PdX_2(PPh_3)_2$  due to its reduction in the diffusion layer. A dynamic concentration should be measured which becomes larger as the scan rate is reduced. If not, thermodynamic equilibrium concentrations can be determined. The ratio  $r = i/i_0$  [*i*: reduction peak current at  $R_1$  of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the presence of 100 equivalents of  $nBu_4NCl; i_0$ : same current but in the absence of added *n*Bu<sub>4</sub>NCl] was then plotted versus the logarithm of the scan rate (Figure 3a).

This ratio clearly does not depend on the scan rate which means that within the time-scale of the cyclic voltammetry investigated here  $(0.2 < v < 20 \text{ V s}^{-1})$ , equilibrium 2 is frozen, so that the thermodynamic concentration of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the equilibrium can be determined by the ratio  $r = i/i_0 = [PdCl_2(PPh_3)_2]_{equil}/[PdCl_2(PPh_3)_2]_0$ . This allows the determination of the equilibrium constant  $K_{Cl}$ . In the present case, the dynamics of equilibrium 2 are not accessible because it would require scan rates much lower than 0.2 V s<sup>-1</sup>, which could not be used since diffusion processes would be contaminated by convection.

## **FULL PAPER**



Figure 3. (a) Variation of the ratio  $r = il_{i_0}$  versus the logarithm of the scan rate (v in V·s<sup>-1</sup>); *i*: reduction peak current at  $R_1$  of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 1.5 mmol·dm<sup>-3</sup> in THF (containing *n*Bu<sub>4</sub>NBF<sub>4</sub>, 0.3 mol·dm<sup>-3</sup>) in the presence of 100 equivalents of *n*Bu<sub>4</sub>NCl;  $i_0$ : same current but in the absence of added *n*Bu<sub>4</sub>NCl at 20 °C; the reduction peak currents were measured at steady gold disk electrodes (i.d. = 0.5 mm for  $v < 5 \text{ V·s}^{-1}$  and i.d. = 0.125 mm for  $v > 5 \text{ V·s}^{-1}$ ; (b) variation of the ratio  $r_D = il_{i_0}$  versus the logarithm of the concentration of *n*Bu<sub>4</sub>NCl; *i*: reduction peak current at  $R_1$  of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 1.5 mmol·dm<sup>-3</sup> in THF (containing *n*Bu<sub>4</sub>NBF<sub>4</sub>, 0.3 mol·dm<sup>-3</sup>) in the presence of *n* equivalents of *n*Bu<sub>4</sub>NCl and 10 equivalents of PPh<sub>3</sub>;  $i_0$ : same current but in the absence of added *n*Bu<sub>4</sub>NCl; the reduction peak currents were measured at a steady gold disk electrode (i.d. = 0.5 mm) with a scan rate of 0.2 V·s<sup>-1</sup> at 20 °C

$$PdX_{2}(PPh_{3})_{2} + X^{-} \implies PdX_{3}(PPh_{3})^{-} + PPh_{3} \quad K_{X} \quad (2)$$
  
at t = 0 C<sub>0</sub> nC<sub>0</sub> 0 0  
at equil. rC<sub>0</sub> (n-1+r)C<sub>0</sub> C<sub>0</sub>(1-r) C<sub>0</sub>(1-r)  
 $\approx nC_{0}$   
$$K_{X} = \frac{[PdX_{3}L^{-}][L]}{[L]} = \frac{(1-r)^{2}}{[L]} \text{ where } n = [X^{-}]_{0}/[PdX_{2}(PPh_{3})_{2}]_{0}$$

$$[PdX_2L_2][X^-]$$
  $n \times r$ 

From this expression one obtains

$$r^2 - 2r(1 + nK_{\rm X}/2) + 1 = 0$$

so that

$$r = 1 + nK_{\rm X}/2 - \{(nK_{\rm X}/2)^2 + nK_{\rm X}\}^{1/2}$$
(4)

The ratio  $r = i/i_0$  was measured for various amounts of X<sup>-</sup> [*n* equivalents/Pd<sup>II</sup>] at a given scan rate. Plotting the experimental value of *r* versus log *n* at a given rate constant and comparison with the theoretical curve should allow the determination of  $K_X$ . However, this calculation is based on the fact that the reduction peak current *i* at  $R_1$  is proportional to the concentration of the species PdX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> which is in fact true if the diffusion coefficient *D* of  $PdX_2(PPh_3)_2$   $(i \propto D^{1/2})^{[12]}$  does not vary with the experimental conditions i.e. when the concentration of *n*Bu<sub>4</sub>NX and consequently the ionic strength increases. This has been checked by performing cyclic voltammetry of PdX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> for X = Cl, Br, I, in the presence of various amounts of  $nBu_4NX$  but with a large excess of PPh<sub>3</sub> (10 equivalents), so that the equilibrium according to Equation 2 was completely shifted to its left-hand side and consequently only the reduction peak  $R_1$  of PdX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was observed. Under these conditions, the reduction peak current *i* of  $PdX_2(PPh_3)_2$ , at a constant scan rate, was found to vary with the concentration of  $nBu_4NX$  (X = Cl, Br). This is illustrated in Figure 3b where the ratio  $r_{\rm D} = i/i_0$  [*i*: reduction peak current at  $R_1$  of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the presence of n equivalents of nBu<sub>4</sub>NCl and 10 equivalents of PPh<sub>3</sub>; i<sub>0</sub>: same current but in the absence of added nBu<sub>4</sub>NCl] was plotted versus log [ $nBu_4NCl$ ]. The ratio  $r_D$  differs from unity at high chloride concentrations. This suggests that the diffusion coefficient of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> is not constant but decreases upon increasing the concentration of chloride ions because of the higher and higher viscosity of the solution. Consequently, the equilibrium constant  $K_X$  was determined as explained above but by plotting the ratio  $i/(i_0 \times r_D)$  instead of  $i/i_0$  versus log *n* (Figure 4). The values of the equilibrium constant  $K_X$  (X = Cl, Br, I) are collected in Table 2.

Table 2. Equilibrium constant  $K_X$  for the equilibrium PdX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> +  $X^- \rightleftharpoons PdX_3$ (PPh<sub>3</sub>)<sup>-</sup> + PPh<sub>3</sub>, with  $nBu_4N^+$  as the countercation at 25 °C

X		Cl	Br	Ι
$\frac{10^{+3}K_{\rm X}}{10^{+3}K_{\rm X}}$	THF	10 (±1)	0.9 (±0.1)	1.7 (±0.3)
	DMF	2 (±1)	n.d.	n.d.



Figure 4. Determination of the equilibrium constant  $K_{\rm Cl}$  (see Equations 2 and 4) in THF at 20 °C; plot of  $i/(i_0 \times r_{\rm D})$  versus the logarithm of *n* (equivalents of *n*Bu<sub>4</sub>NCl); *i*: reduction peak current at  $R_1$  of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 1.5 mmol·dm<sup>-3</sup> in THF (containing *n*Bu<sub>4</sub>NBF<sub>4</sub>, 0.3 mol·dm<sup>-3</sup>) in the presence of various amounts of *n*Bu<sub>4</sub>NCl; *i*<sub>0</sub>: same current but in the absence of added *n*Bu<sub>4</sub>NCl; the reduction peak currents were measured at a steady gold disk electrode (i.d. = 0.5 mm) with a scan rate of 0.2 V·s<sup>-1</sup>; for the definition of  $r_{\rm D}$  see caption of Figure 3b; the solid lines are the theoretical predictions according to Equation 4

The equilibrium constant  $K_{Cl}$  has been determined at different temperatures in THF. The equilibrium according to Equation 2 favors production of the anionic species at higher temperatures. The Arrhenius plot of  $\ln K_{Cl}$  versus 1/ T (Figure 5) allows the determination of the activation par-

## **FULL PAPER**

ameters from the slope and intercept, so that  $\Delta H^0 = 20 \text{ kJ} \text{ mol}^{-1}$  and  $\Delta S^0 = -20 \text{ J} \text{ K}^{-1}$ .



Figure 5. Arrhenius plot for the equilibrium  $PdCl_2(PPh_3)_2 + Cl^- \Rightarrow PdCl_3(PPh_3)^- + PPh_3$  (with  $nBu_4N$  as counter-cation) in THF containing  $nBu_4NBF_4$  (0.3 mol·dm<sup>-3</sup>); variation of ln  $K_{Cl}$  versus 1/T

The small value of  $\Delta S^0$  is indicative of a reaction in which there is no variation of the numbers of species in solution.

#### **Miscellaneous Reactions**

All reactions investigated above concern the substitution of the phosphane ligand by the same halide X<sup>-</sup> as those present in PdX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. Reactions are more complicated when different halides are considered. For example: when 30 equivalents of  $nBu_4NI$  were added to a solution of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2.4 mmol·dm<sup>-3</sup>) in THF, PPh<sub>3</sub> was detected in the <sup>31</sup>P-NMR spectrum as a narrow signal indicative of the substitution of the phosphane ligand by one iodide ion which generates anionic species: PdCl<sub>2</sub>I(PPh<sub>3</sub>)<sup>-</sup>.

$$PdCl_2(PPh_3)_2 + I^- \rightarrow PdCl_2I(PPh_3)^- + PPh_3$$
(5)

However, this complex could not be characterized since an unresolved broad signal was present at  $\delta = 17.5$  suggesting that scrambling reactions occurred by equilibria such as in Equation 6 and/or 7.

 $PdCl_2I(PPh_3)^- + PPh_3 \implies PdICl(PPh_3)_2 + Cl^-$  (6)

$$PdCl_2(PPh_3)_2 + I^{-} \implies PdICl(PPh_3)_2 + Cl^{-}$$
(7)

Under these conditions, several neutral or anionic complexes may be formed:  $PdICl(PPh_3)_2$ ,  $PdI_2(PPh_3)_2$ ,  $PdCl_2I(PPh_3)^-$ ,  $PdClI_2(PPh_3)^-$ ,  $PdI_3(PPh_3)^-$  involved in different and simultaneous equilibria, responsible for the unresolved broad signal observed in the <sup>31</sup>P-NMR spectrum.

## **Discussion and Conclusion**

Halide ions can substitute a phosphane ligand in  $PdX_2(PPh_3)_2$  complexes to afford anionic species  $PdX_3(PPh_3)^-$  by an equilibrium. Similar anionic  $NiCl_3(PR_3)^-$  (R = isopropyl) complexes have been reported to be formed by phosphane substitution<sup>[13]</sup> while  $PtCl_3(PR_3)^-$  complexes are usually synthesized by allowing chloride ions to react with phosphane-deficient dimeric

complexes,  $Pt_2Cl_4(PR_3)_2$ .<sup>[14]</sup> However,  $PdX_2(PPh_3)_2$  remains the more stable complex in THF and DMF for moderate halide ion concentrations. The phosphane substitution is easier for chloride ions which reveals the higher nucleophilic affinity of Cl<sup>-</sup> for the palladium(II) center than that of Br<sup>-</sup> or I<sup>-</sup>. This can be understood as an interaction between "hard" Lewis acids and bases. The substitution of the phosphane by the chloride is more efficient in THF than in DMF probably due to the lower capacity of THF relative to DMF to solvate chloride ions compared to the larger anionic species PdX<sub>3</sub>L<sup>-</sup>.

Conversely, we have reported that the affinity of Cl<sup>-</sup> for palladium(0) centers is less than that of  $Br^-$  or  $I^-$  which can be rationalized as an interaction between "soft" centers.<sup>[3]</sup> Those results evidence the ability of halide ions to coordinate both palladium(0) and palladium(II) complexes and thus probably to influence further reactions involving such complexes. We have already reported the consequences of the ligation of palladium(0) complexes by halide<sup>[3-5]</sup> or acetate ions<sup>[5][15]</sup> on the mechanism of palladium-catalyzed reactions. Although palladium(II) dihalide complexes are less involved as promoters of catalytic reactions than palladium(0) complexes, arylpalladium(II) halide complexes are postulated to be crucial intermediates in palladium(0)catalyzed reactions involving aryl halides. Reactions of halide ions  $X'^-$  with ArPdX(PPh<sub>3</sub>)<sub>2</sub> complexes do not result in a substitution of one phosphane ligand but rather substitution of the halide  $X^-$  to form neutral ArPdX'(PPh<sub>3</sub>)<sub>2</sub> complexes.<sup>[16]</sup> In fact, we have established that ArPdX(PPh<sub>3</sub>)<sub>2</sub> complexes are not reactive intermediates in cross-coupling<sup>[3][5]</sup> or Heck<sup>[5][15]</sup> reactions and the effect of chloride or acetate anions on the course of these reactions is to produce new anionic or neutral complexes such as  $ArPdX(Cl)(PPh_3)_2^-$ ,  $ArPdX(OAc)(PPh_3)_2^-$ , ArPd(OAc)- $(PPh_3)_2$  where the two phosphane ligands remain attached to the palladium(II) center

## **Experimental Section**

**General:** <sup>31</sup>P-NMR spectra were recorded with a Bruker W 400 spectrometer (162 MHz) with  $H_3PO_4$  as an external reference. Cyclic voltammetry was performed with a home-made potentiostat and a waveform generator Tacussel GSTP4 or EGG. The cyclic voltammograms were recorded with a Nicolet 301 oscilloscope.

**Chemicals:** DMF was distilled from calcium hydride under vacuum and kept under argon. Commercial  $nBu_4NCl$ ,  $nBu_4NBr$ ,  $nBu_4NI$ (Acros) were used after crystallisation. They were melted and dried under vacuum. PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PdBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PdI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, was prepared according to described procedures.<sup>[17]</sup>

Electrochemical Set Up and Electrochemical Procedure for Cyclic 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<sup>2</sup> apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge filled with 3 mL of THF or DMF containing  $nBu_4NBF_4$  (0.3 mol·dm<sup>-3</sup>).

**General Procedure:** 12 mL of THF or DMF containing  $nBu_4NBF_4$ (0.3 mol·dm<sup>-3</sup>) was poured into the cell followed by PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (16.8 mg, 0.024 mmol) and various amounts of nBu<sub>4</sub>NCl. Cyclic voltammetry was performed at steady gold disk electrodes with various scan rates.

- <sup>31</sup>P-NMR spectrum at  $\delta = 27.42$  similar to the signal of the complex formed in Equation 1.
- <sup>[8]</sup> R. J. Goodfellow, P. L. Goggin, D. A. Duddell, J. Chem. Soc. A 1968, 504-506.
- <sup>[9]</sup> J. Chatt, L. M. Venanzi, J. Chem. Soc. 1957, 2351-2356.
- [10] R. Bardi, A. M. Piazzesi, A. Del Pra, G. Cavinato, L. Toniolo, Inorg. Chim. Acta 1983, 75, 15–19.
   [11] A. J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley,
- New York, **1980**, p. p. 443–449. <sup>[12]</sup> A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, Wiley,
- New York, **1980**, p. 213–248. <sup>[13]</sup>  $[^{13a]}$  G. G. Eberhardt, W. P. Griffin, *J. Catal.* **1970**, *16*, 245–253.  $[^{13b]}$  Y. Chauvin, unpublished results, personal communication, 1996.
- [14] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, B. F. Taylor, I. R. H. Marshall, J. Chem. Soc., Dalton Trans. 1976, 459–467.
- K. H. Marshall, J. Chem. Soc., Dation Trans. 1710, 437–401.
   [15] C. Amatore, E. Carré, A. Jutand, M. A. M'Barki, G. Meyer, Organometallics 1995, 14, 5605–5614.
   [16] M. C. Pilon, V. V. Grushin, Organometallics 1998, 17, 1774–1781.
- <sup>[17]</sup> F. R. Hartley, Organomet. Chem. Rev., Sect. A 1970, 6, 119. Received January 7, 1999 [I99007]
- <sup>[1]</sup> E. I. Negishi, T. Takahashi, K. Akiyoshi, J. Chem. Soc., Chem. Commun. 1986, 1338-1339.
- C. Amatore, M. Azzabi, A. Jutand, J. Organomet. Chem. 1989, 363, C41-C45. [2]
- <sup>[3]</sup> C. Amatore, M. Azzabi, A. Jutand, J. Am. Chem. Soc. 1991, 113, 1670–1677.
  <sup>[4]</sup> C. Amatore, A. Jutand, A. Suarez, J. Am. Chem. Soc. 1993, 115, 9531–9541.
- [5]
- For a review see: C. Amatore, A. Jutand, J. Organomet. Chem. 1999, 573, 254–278.
- [7]
- L. Mottier, part of Ph.D. thesis, University Paris VII, **1995**.  $[PdCl_3(PPh_3)^-$ ,  $nBu_4N^+]$  has been synthesized independently by treating Pd<sub>2</sub>Cl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> with two equivalents of  $nBu_4NCl$ , in THF according to a reported procedure:<sup>[8]</sup> Pd<sub>2</sub>Cl<sub>4</sub>-(PPh<sub>3</sub>)<sub>2</sub> + 2 Cl<sup>-</sup>  $\rightarrow$  2 PdCl<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup>. It was characterized by its