Rate and Mechanism of the Oxidative Addition of Benzoic Anhydride to Palladium(0) Complexes in DMF

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The rate constant of the oxidative addition of the benzoic anhydride $(PhCO)_2O$ to $[Pd^0(PPh_3)_4]$ has been determined in DMF and compared to that of phenyl halides and phenyl triflate. The following reactivity order has been established: $PhI \gg (PhCO)_2O > PhOTf > PhBr$. The oxidative addition of $(PhCO)_2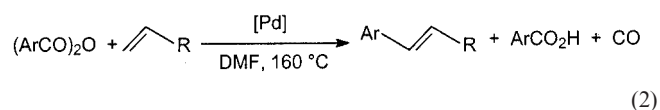O$ proceeds by activation of one C–O bond. Two acyl-Pd^{II} complexes are formed: a neutral complex $trans$-$[(PhCO)Pd(OCOPh)(PPh_3)_2]$ and a cationic complex $trans$-$[(PhCO)PdS(PPh_3)_2]^+$ (S = DMF) showing that the decarbonylation process is highly endergonic. The exchange of PPh_3 by the bidentate ligand dppp does not favor the decarbonylation process.

Introduction

Aromatic carboxylic anhydrides $(ArCO)_2O$ were first used by Sakamoto et al. as *acylating* agents in palladium-catalyzed cross-coupling reactions [Equation (1)]:[1]
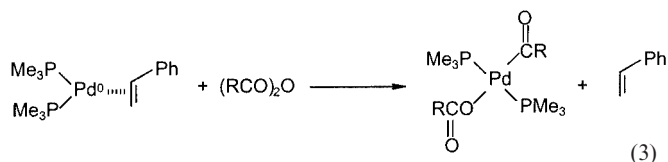
$$(ArCO)_2O \ + \ Ar'ZnX \ \xrightarrow[\text{THF, rt}]{Pd^0(PPh_3)_4} \ ArCOAr' \ + \ ArCO_2ZnX$$

$$(1)$$
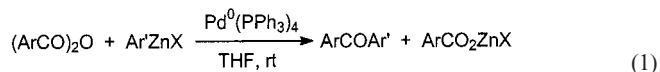
Recently, they have also been used by de Vries et al. as *arylating* agents in palladium-catalyzed Heck reactions [Equation (2)]:[2]

$$(ArCO)_2O \ + \ \diagup\!\!\diagdown R \ \xrightarrow[\text{DMF, 160 °C}]{[Pd]} \ Ar\diagup\!\!\diagdown\!\!\diagup R \ + \ ArCO_2H \ + \ CO$$

$$(2)$$

When compared to the aryl halides or triflates more commonly used as arylating agents in Heck reactions,[3–5] aromatic carboxylic anhydrides appear to be more attractive since they are a cheap aryl source and they do not lead to the formation of environmentally wasteful halide salts. Moreover, no base is required, as it usually is in Heck reactions, since benzoate anions are released in the reaction. They serve as a base by forming aromatic carboxylic acid, which can be recycled back to the aromatic carboxylic anhydride. CO is then the only by-product of the Heck reaction [Equation (2)].

By analogy to aryl halides and triflates,[3–5] the first step of the catalytic cycle of the Heck reaction must be an oxidative addition of the aromatic carboxylic anhydride to the palladium(0) catalyst, giving a palladium(II) complex. Further transformation of this complex gives an intermediate aryl-Pd^{II} complex able to react with the alkene. The oxidative addition of carboxylic anhydrides to palladium(0) complexes has been reported by Yamamoto et al.[6–8] It proceeds by cleavage of one C–O bond and *trans*-acyl(carboxylato)palladium(II) complexes have been isolated and characterized with the PMe$_3$ ligand [Equation (3), (R = alkyl or phenyl)].[6,7]

$$\begin{array}{c}\text{Me}_3\text{P} \\ \quad\ \ \diagdown \\ \quad\ \ \ \text{Pd}^0\!\cdots\!\| \\ \quad\ \ \diagup \\ \text{Me}_3\text{P} \end{array}\!\!\text{Ph} \ + \ (RCO)_2O \ \longrightarrow \ \begin{array}{c} \text{Me}_3\text{P} \quad \overset{O}{\overset{\|}{C}}R \\ \diagdown\ \ \diagup \\ \ \ \text{Pd} \\ \diagup\ \ \diagdown \\ \text{RCO}\ \ \ \text{PMe}_3 \\ \ \ \|\ \ \\ \ \ O \end{array} \ + \ \diagup\!\!\diagdown\!\!\|\ \text{Ph}$$

$$(3)$$

The reactivity of such complexes has been investigated by the same group. Hydrogenation gives $RCHO$ and RCO_2H, establishing that no decarbonylation occurs in the acyl(carboxylato)palladium(II) complex formed in the oxidative addition.[6,7] Hydrogenation of $(PhCO)_2O$ to form PhCHO and $PhCO_2H$ has been successfully developed in THF with $[Pd^0(PPh_3)_4]$ as a catalyst.[6–8] Only one reaction in the aromatic series is reported (phthalic anhydride, PMe$_3$ as the ligand), where CO is released from the acyl(carboxylato)palladium(II) complex, giving rise to the formation of an aryl(carboxylato)Pd^{II} complex.[7]

Grushin and Alper have characterized in solution the complex *trans*-$[(PhCO)Pd(OCOPh)(PCy_3)_2]$ formed by reacting $(PhCO)_2O$ with $[Pd^0(PCy_3)_2]$ (Cy = cyclohexyl).[9] Decarbonylation was observed in the course of the oxidative addition as a very minor process (5–10%).

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We report here a mechanistic investigation of the oxidative addition of benzoic anhydride $(PhCO)_2O$ to $[Pd^0(PPh_3)_4]$ in DMF (solvent of the Heck reaction). The objective is to compare its reactivity to that of phenyl halides and phenyl triflate and to characterize the Pd^{II} complex(es) generated in the oxidative addition.
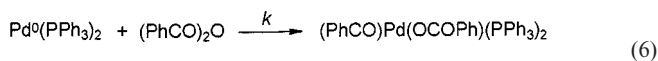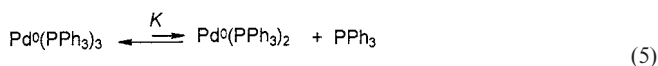
Results and Discussion

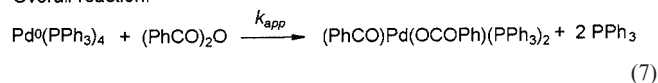### Rate of the Oxidative Addition of Benzoic Anhydride $(PhCO)_2O$ to $Pd^0(PPh_3)_4$ in DMF

The kinetics of the oxidative addition of $(PhCO)_2O$ to $[Pd^0(PPh_3)_4]$ $(C_0 = 1.33\ mM)$ in DMF (containing nBu_4NBF_4, 0.3 M) was monitored by amperometry at a rotating gold disk electrode, as reported for aryl halides[10] and triflates.[11] $[Pd^0(PPh_3)_3]$, the main complex generated in DMF from $[Pd^0(PPh_3)_4]$ [Equation (4)], exhibited an oxidation peak at $+0.11$ V vs. SCE. The rotating disk electrode was polarized at $+0.35$ V, on the plateau of the oxidation wave of $[Pd^0(PPh_3)_3]$. The kinetics of the oxidative addition of $(PhCO)_2O$ was monitored by recording the decay of the oxidation current, i, of $[Pd^0(PPh_3)_3]$ (proportional to the Pd^0 concentration) as a function of time, up to 100% conversion. The reaction was rather slow at 25 °C and the kinetic investigation was then performed at 40 °C.

$$Pd^0(PPh_3)_4 \longrightarrow Pd^0(PPh_3)_3 + PPh_3 \qquad (4)$$
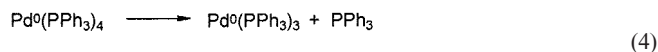
It is well established that when $[Pd^0(PPh_3)_4]$ is the Pd^0 precursor, any oxidative addition (e.g. of aryl halides or triflates) proceeds from the 14-electron complex $[Pd^0(PPh_3)_2]$ [Equation (5) and (6)].[10,11] The Pd^{II} complex formed in the oxidative addition is tentatively written as $[(PhCO)Pd(OCOPh)(PPh_3)_2]$ after cleavage of one C−O bond, by analogy to the complex obtained when the Pd^0 is ligated by PMe_3 [6,7] or by PCy_3.[9] Its structure will be established in the second part of this work.

$$Pd^0(PPh_3)_3 \underset{K}{\rightleftharpoons} Pd^0(PPh_3)_2 + PPh_3 \qquad (5)$$

$$Pd^0(PPh_3)_2 + (PhCO)_2O \xrightarrow{k} (PhCO)Pd(OCOPh)(PPh_3)_2 \qquad (6)$$

Overall reaction:

$$Pd^0(PPh_3)_4 + (PhCO)_2O \xrightarrow{k_{app}} (PhCO)Pd(OCOPh)(PPh_3)_2 + 2\ PPh_3 \qquad (7)$$

The kinetic investigation allows the determination of the apparent rate constant k_{app} of the overall oxidative addition [Equation (7)]. Due to the continuous release of PPh_3 in the fast equilibrium (5) during the course of the oxidative addition, the kinetic law is expressed in Equation (8) $\{C_0:$ initial concentration of $[Pd^0(PPh_3)_4]$, $(PhCO)_2O$ in large excess$\}$.[10]

$$2\ln([Pd^0]/[Pd^0]_0) + 1 - [Pd^0]/[Pd^0]_0 = -Kk[(PhCO)_2O]t/C_0 = -k_{app}[(PhCO)_2O]t = -k_{obs}t \qquad (8)$$

The plot of $2\ln(i/i_0) + 1 - i/i_0 = 2\ln([Pd^0]/[Pd^0]_0) + 1 - [Pd^0]/[Pd^0]_0$ versus time is a straight line (Figure 1a) (i: oxidation current of Pd^0 at t; i_0: initial oxidation current). The value of k_{obs} was calculated from the slope of the regression line [Equation (8)]. The benzoic anhydride concentration was varied in the range $0.01-0.4$ M and the plot of the corresponding k_{obs} value versus the benzoic anhydride concentration gave a straight line (Figure 1b). The reaction order in benzoic anhydride is thus $+1$ [Equation (8)]. This establishes that the mechanism of the oxidative addition of the benzoic anhydride to $[Pd^0(PPh_3)_4]$ [Equations (4−7)] is the same as that already established for aryl halides and triflates.[10,11] The value of $Kk = 3.6 \times 10^{-5}\ s^{-1}$ was calculated from the slope of the regression line of Figure 1b and allows the calculation of the apparent rate constant of the overall reaction [Equation (7)]: $k_{app} = Kk/C_0$ (in $M^{-1}s^{-1}$)
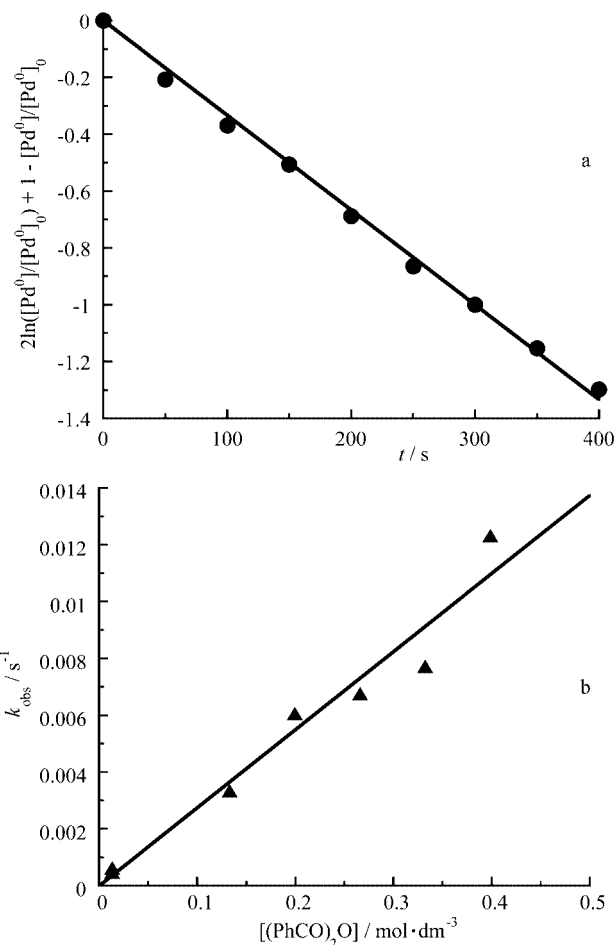

Figure 1. Oxidative addition of $(PhCO)_2O$ in DMF (containing nBu_4NBF_4 0.3 M) to $[Pd^0(PPh_3)_4]$ (1.33 mM) at 40 °C, monitored by amperometry at a rotating gold disk electrode (diameter: 2 mm, $\omega = 105$ rad s^{-1}) polarized at $+0.35$ V vs. SCE; a) $[(PhCO)_2O] = 0.133$ M; plot of $2\ln(i/i_0) + 1 - i/i_0 = 2\ln([Pd^0]/[Pd^0]_0) + 1 - [Pd^0]/[Pd^0]_0$ versus time (i: oxidation current of $[Pd^0(PPh_3)_3]$ at t; i_0: initial oxidation current). k_{obs} (s^{-1}) is calculated from the slope [Equation (8)]; b) Plot of k_{obs} (s^{-1}) versus $(PhCO)_2O$ concentration

Table 1. Comparative reactivity of $(PhCO)_2O$, PhI, PhBr and PhOTf in their oxidative addition to $[Pd^0(PPh_3)_4]$ (2 mM) in DMF [Equation (7)] for $(PhCO)_2O$]

	T (°C)	PhI	$(PhCO)_2O$	PhOTf	PhBr
k_{app} ($M^{-1}s^{-1}$)	25	25	3.1×10^{-3}	–	–
k_{app} ($M^{-1}s^{-1}$)	40	–	1.8×10^{-2}	1.2×10^{-2}	10^{-2}

[Equation (8)], for any value of C_0 (Table 1). It is worthwhile to note that, even at the lowest benzoic anhydride concentration investigated here (0.013 M), the oxidation current of Pd^0, and therefore the concentration of Pd^0, dropped to almost zero. This indicates that the oxidative addition went to completion and that the reverse reaction, the formation of $(PhCO)_2O$ and a Pd^0L_2 complex by reductive elimination from $[(PhCO)Pd(OCOPh)(PPh_3)_2]$,[9,12] was much slower than the rate of the oxidative addition and did not interfere in the kinetics investigated herein.

Since aromatic carboxylic anhydrides appear to be an alternative to the use of aryl halides and triflates in Heck reactions,[2] it was of interest to compare their reactivity in the oxidative addition, which may be rate determining in the case of poorly reactive aryl derivatives. The apparent rate constant k_{app} of the oxidative addition of PhOTf and PhBr to $[Pd^0(PPh_3)_4]$ has also been determined at 40 °C, in DMF, to allow comparison with that of $(PhCO)_2O$ (Table 1). The order of reactivity in DMF has been established to be:

$$PhI >> (PhCO)_2O > PhOTf > PhBr$$

When considering the oxidative addition, $(PhCO)_2O$ is thus slightly more reactive than PhOTf and PhBr and may therefore be a good alternative to the use of PhOTf or PhBr in any reaction where the oxidative addition is rate determining, provided the subsequent decarbonylation takes place.

Palladium(II) Complexes Generated in the Oxidative Addition of Benzoic Anhydride $(PhCO)_2O$ to $Pd^0(PPh_3)_4$ in DMF

The oxidative addition of $(PhCO)_2O$ to $[Pd^0(PPh_3)_4]$ in DMF at 40 °C was monitored by conductivity measurements, which allows the characterization of ionic complexes as well as their rate of formation.[11] Starting with a residual conductivity $\kappa_0 = 5$ μS·cm^{-1}, we observed that the conductivity of the solution increased as soon as $(PhCO)_2O$ (100 equiv.) was added to $[Pd^0(PPh_3)_4]$ ($C_0 = 1.33$ mM) in DMF, attesting that an ionic complex was formed in the very first stages of the oxidative addition (Figure 2). From the kinetic curve of Figure 2, we see that at least two different ionic species are formed successively, at different time scales, the first complex being formed on a shorter time scale ($t < 800$ s) than the second one. The first time scale is compatible with that of the oxidative addition when monitored independently by amperometry ($t_{1/2} = 250$ s, see Figure 1a).

This suggests that the neutral complex $[(PhCO)Pd(OCOPh)(PPh_3)_2]$, initially formed in the oxidative addition [Equation (7)], dissociates to give a cationic complex $[(PhCO)PdS(PPh_3)_2]^+$ (S = DMF) [Equation (9)] in a reaction which is faster than the oxidative addition.[13,14] A second ionic species is then generated in a subsequent reaction. This latter might be a decarbonylation as in Equation (10) or any decomposition process leading to more conductive ionic species {e.g., formation of a phosphonium salt $PhCOO-PPh_3^+$ via a reductive elimination from $[(PhCO)Pd(OCOPh)(PPh_3)_2]$,[15] reaction of dioxygen with $[(PhCO)PdS(PPh_3)_2]^+$,[16] etc.}.
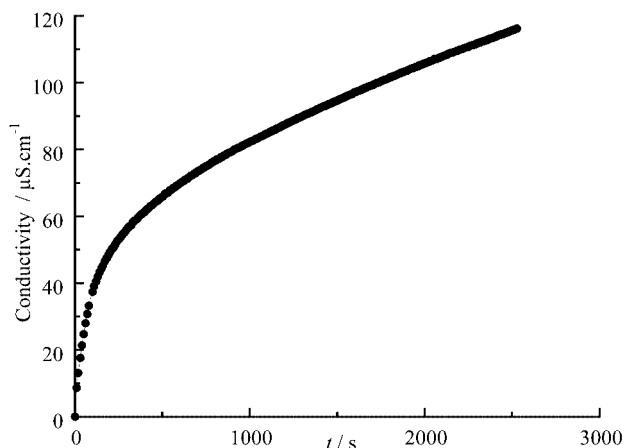
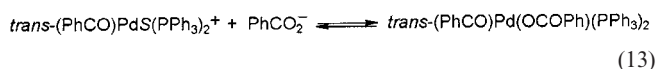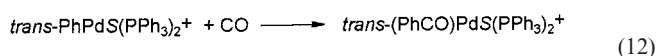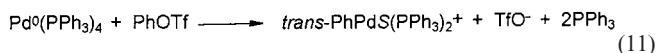Figure 2. Oxidative addition of $(PhCO)_2O$ (0.133 M) to $[Pd^0(PPh_3)_4]$ (1.33 mM) in DMF at 40 °C, monitored by conductivity measurements; variation of the conductivity *versus* time

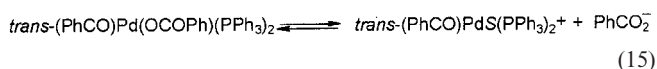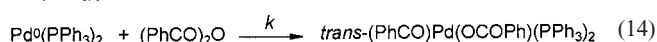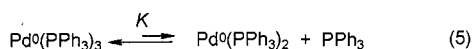$$(PhCO)Pd(OCOPh)(PPh_3)_2 \rightleftharpoons (PhCO)PdS(PPh_3)_2^+ + PhCO_2^- \quad (9)$$

$$(PhCO)PdS(PPh_3)_2^+ \rightleftharpoons CO + PhPdS(PPh_3)_2^+ \quad (10)$$
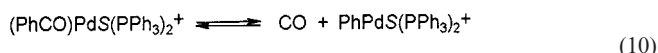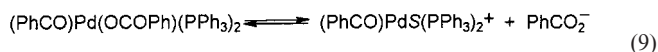
To test the hypotheses formulated in Equation (9) and (10), the oxidative addition of $(PhCO)_2O$ to $[Pd^0(PPh_3)_4]$ was monitored by ^{31}P NMR spectroscopy[17] in DMF to characterize the formed Pd^{II} complexes. The ^{31}P NMR spectroscopy was first investigated after the amperometry experiment, i.e., when the oxidative addition, performed with $[Pd^0(PPh_3)_4]$ ($C_0 = 1.33$ mM) and $(PhCO)_2O$ (100 equiv.) in DMF at 40 °C, was over (experiment A). The ^{31}P NMR spectrum exhibited three main singlets: one singlet at $\delta = -5.4$ ppm characteristic of free PPh_3 released during the oxidative addition [Equation (7)], one singlet at $\delta = 25.6$ ppm characteristic of $(O)PPh_3$ [16] and one singlet at $\delta_1 = 19.9$ ppm, which then characterizes the major complex formed in the oxidative addition. Two smaller singlets were also observed at $\delta_2 = 20.4$ ppm and $\delta_3 = 24.1$ ppm (each with a magnitude of ca. 15% of that of the singlet at δ_1). In a second experiment, the oxidative addition was monitored in an NMR tube at room temperature, starting from a more concentrated solution of $[Pd^0(PPh_3)_4]$ ($C_0 = 7$ mM) and $(PhCO)_2O$ (100 equiv.) in DMF (experiment B). After 30 min, the ^{31}P NMR spectrum exhibited, besides some un-

changed $[Pd^0(PPh_3)_3]$ ($\delta = 10.7$ ppm), the two singlets δ_1 and δ_2 already observed in experiment A, although here the singlet at δ_2 was the major one (relative integration of 0.4:1). After 3 hours, the two singlets δ_1 and δ_2 had almost the same magnitude. This indicates that the signal at $\delta_2 = 20.4$ ppm characterizes the first complex formed in the oxidative addition, which then gives a second complex at $\delta_1 = 19.9$ ppm. Those two complexes are ligated by two PPh_3 ligands sitting in a *trans* position in the Pd^{II} complexes because only singlets were detected. The signal at $\delta_3 = 24.1$ ppm was also detected with a magnitude of half that of δ_1, i.e., in larger amount than in experiment A.

In order to assign the signals at δ_1 and δ_2 to the complexes postulated in Equation (9) and (10), i.e., [(PhCO)-Pd(OCOPh)(PPh$_3$)$_2$], [(PhCO)PdS(PPh$_3$)$_2$]$^+$ or [PhPdS(PPh$_3$)$_2$]$^+$, these complexes were synthesized independently in DMF following known procedures. An oxidative addition was performed with PhOTf (100 equiv.) and $[Pd^0(PPh_3)_4]$ ($C_0 = 7$ mM) in DMF and monitored by ^{31}P NMR spectroscopy. Such a reaction is known to give, in DMF, the cationic complex *trans*-[PhPdS(PPh$_3$)$_2$]$^+$·[OTf]$^-$ [Equation (11)].[11] This complex exhibits a singlet at $\delta = 21.9$ ppm (Table 2, entry 1) different from δ_1 and δ_2. We can already assume, therefore, that the cationic complex *trans*-[PhPdS(PPh$_3$)$_2$]$^+$, postulated in Equation (10), is not formed in the oxidative addition of (PhCO)$_2$O under the experimental conditions used above. When CO was bubbled into the NMR tube, a new singlet appeared at higher field at $\delta = 20.0$ ppm and was assigned to *trans*-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ [Equation (12), Table 2, entry 2].[18,19] This latter signal is very similar to the signal at δ_1 observed when the oxidative addition was performed with (PhCO)$_2$O (experiments A and B, Table 2, entry 3). When PhCO$_2^-$·Li$^+$ was then added in large excess into the NMR tube, a singlet appeared at $\delta = 20.4$ ppm and was assigned to *trans*-[(PhCO)Pd(OCOPh)(PPh$_3$)$_2$] [Equation (13)].[20] This latter signal is the same as the signal at δ_2 observed when the oxidative addition was performed with (PhCO)$_2$O (experiment A and B, Table 2, entry 4).

$$Pd^0(PPh_3)_4 + PhOTf \longrightarrow \textit{trans-}PhPdS(PPh_3)_2^+ + TfO^- + 2PPh_3 \qquad (11)$$

$$\textit{trans-}PhPdS(PPh_3)_2^+ + CO \longrightarrow \textit{trans-}(PhCO)PdS(PPh_3)_2^+ \qquad (12)$$

$$\textit{trans-}(PhCO)PdS(PPh_3)_2^+ + PhCO_2^- \rightleftharpoons \textit{trans-}(PhCO)Pd(OCOPh)(PPh_3)_2 \qquad (13)$$

Consequently, two complexes are formed in the oxidative addition of (PhCO)$_2$O to $[Pd^0(PPh_3)_4]$: *trans*-[(PhCO)-Pd(OCOPh)(PPh$_3$)$_2$] and *trans*-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ {see Equation (5) and Equation (14) and (15) for the mechanism of the oxidative addition of benzoic anhydride to $[Pd^0(PPh_3)_4]$ in DMF}.

$$Pd^0(PPh_3)_3 \underset{}{\overset{K}{\rightleftharpoons}} Pd^0(PPh_3)_2 + PPh_3 \qquad (5)$$

$$Pd^0(PPh_3)_2 + (PhCO)_2O \overset{k}{\longrightarrow} \textit{trans-}(PhCO)Pd(OCOPh)(PPh_3)_2 \qquad (14)$$

$$\textit{trans-}(PhCO)Pd(OCOPh)(PPh_3)_2 \rightleftharpoons \textit{trans-}(PhCO)PdS(PPh_3)_2^+ + PhCO_2^- \qquad (15)$$

The fact that *trans*-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ was detected in larger amounts than *trans*-[(PhCO)Pd(OCOPh)(PPh$_3$)$_2$] in experiment A as opposed to experiment B (vide supra) is due to the difference of concentration. In experiment B, the concentration of $[Pd^0(PPh_3)_4]$ was higher than that in experiment A. Consequently the concentration of the released PhCO$_2^-$ was higher in experiment B and Equation (15) was shifted more towards the left hand-side, i.e., to the formation of *trans*-[(PhCO)Pd(OCOPh)(PPh$_3$)$_2$]. This is why *trans*-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ appeared as the major complex at low $[Pd^0(PPh_3)_4]$ concentration (experiment A).

The singlet at $\delta = 24.3$ ppm remained unassigned. Two phenyl-Pd^{II} complexes *trans*-[PhPdS(PPh$_3$)$_2$]$^+$ and *trans*-[PhPd(OCOPh)(PPh$_3$)$_2$] could have been formed by decarbonylation of *trans*-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ and *trans*-[(PhCO)Pd(OCOPh)(PPh$_3$)$_2$], respectively, but the cationic complex *trans*-[PhPdS(PPh$_3$)$_2$]$^+$ was not detected in the NMR spectrum (vide supra). We have independently

Table 2. ^{31}P NMR shifts δ (101 MHz, DMF, [D$_6$]acetone (10%), H$_3$PO$_4$) of phenyl- and acyl-palladium(II) complexes

Entry	Complexes (S = DMF)	δ
1	*trans*-[PhPdS(PPh$_3$)$_2$]$^+$ [a]	21.9 (s)
2	*trans*-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ [b]	20.0 (s)
3	*trans*-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ [c]	19.9 (s)
4	*trans*-[(PhCO)Pd(OCOPh)(PPh$_3$)$_2$][d]	20.4 (s)
5	*trans*-[PhPd(OCOPh)(PPh$_3$)$_2$][e]	21.6 (s)
6	[PhPdS(dppp)]$^+$ [f]	25.2 (d, $J_{P,P}$ = 51 Hz), −2.2 (d, $J_{P,P}$ = 51 Hz)
7	[(PhCO)PdS(dppp)]$^+$ [g]	5.1 (br. d, $J_{P,P}$ = 74 Hz), −8.4 (br. d, $J_{P,P}$ = 74 Hz)
8	[(PhCO)PdS(dppp)]$^+$ [h]	5.1 (d, $J_{P,P}$ = 74 Hz), −8.8 (d $J_{P,P}$ = 74 Hz)
9	[(PhCO)Pd(OCOPh)(dppp)][i]	12.5 (d, $J_{P,P}$ = 72 Hz), −7.9 (d, $J_{P,P}$ = 72 Hz)
10	[PhPd(OCOPh)(dppp)][j]	18.9 (d, $J_{P,P}$ = 51 Hz), −6.5 (d, $J_{P,P}$ = 51 Hz)

[a] Authentic sample with OTf$^-$ as the counter anion. [b] Formed by reaction (12) with OTf$^-$ as the counter anion. [c] Formed in the oxidative addition of benzoic anhydride and [Pd(PPh$_3$)$_4$] with PhCO$_2^-$ as the counter anion. [d] Formed in the oxidative addition of benzoic anhydride and [Pd(PPh$_3$)$_4$] [Equation (7)] and by reaction (13). [e] Formed by reaction of benzoate anion with [PhPdBr(PPh$_3$)$_2$]. [f] Authentic sample with BF$_4^-$ as the counter anion. [g] Formed by reaction (16) with BF$_4^-$ as the counter anion. [h] Formed by reactions (17−19) with PhCO$_2^-$ as the counter anion. [i] Formed by ligand exchange (Scheme 1) and by reaction (18). [j] Formed by reaction (17).

checked that the complex trans-[PhPd(OCOPh)(PPh$_3$)$_2$] was not formed in the oxidative addition, by reacting trans-[PhPdBr(PPh$_3$)$_2$] (δ = 24.2 ppm) with PhCO$_2^-$·Li$^+$ in DMF to induce the Br$^-$/PhCO$_2^-$ substitution.[21] Indeed, a new singlet assigned to trans-[PhPd(OCOPh)(PPh$_3$)$_2$][23] appeared at δ = 21.6 ppm (Table 2, entry 5), which was never observed in the course of the oxidative addition of the benzoic anhydride. Consequently, the decarbonylation must be a very endergonic process, since even at 100 °C for 1 h, under continuous degassing, none of the signals of either trans-[PhPd(OCOPh)(PPh$_3$)$_2$] or trans-[PhPdS(PPh$_3$)$_2$]$^+$ were detected. In contrast, carbonylation of [PhPd(OCOPh)(PPh$_3$)$_2$][20] or trans-[PhPdS(PPh$_3$)$_2$]$^+$ [Equation (12)] proved to be efficient.[22] Consequently, the singlet at δ = 24.3 ppm, which must be due to a decomposition product, remains unassigned.

The influence of the ligand on the decarbonylation process was tested by switching from the monodentate ligand PPh$_3$ investigated above to the bidentate bisphosphane ligand 1,3-bis(diphenyl)phosphanylpropane (dppp). Whereas the acyl group of acyl-Pd^{II} complexes ligated by two monophosphane ligands sits in a cis position relative to each monophosphane ligand, it must sit in a trans position relative to one P of a bidentate bisphosphane ligand. This may affect the decarbonylation process. The oxidative addition of (PhCO)$_2$O to [Pd^0(dba)(dppp)] generated from Pd^0(dba)$_2$ + 1 equiv. dppp was very sluggish. Consequently, one equiv. dppp was added to the solution of trans-[PhCOPdS(PPh$_3$)$_2$]$^+$ and trans-[PhCOPd(OCOPh)(PPh$_3$)$_2$], generated from the oxidative addition of (PhCO)$_2$O to [Pd(PPh$_3$)$_4$], in DMF, to test the effect of the bidentate ligand on the decarbonylation process. The two singlets δ_1 = 19.9 ppm and δ_2 = 20.4 ppm of trans-[PhCOPdS(PPh$_3$)$_2$]$^+$ and trans-[PhCOPd(OCOPh)(PPh$_3$)$_2$], respectively, disappeared. The signal of free PPh$_3$ was observed at δ = −5.4 ppm but not that of dppp (δ = −17.0 ppm), confirming the ligand exchange. As a result of this exchange, a single complex was observed, characterized by two doublets at δ_4 = 12.5 ppm (d, J_{PP} = 72 Hz) and δ_5 = 7.9 ppm (d, J_{PP} = 72 Hz) (Scheme 1).

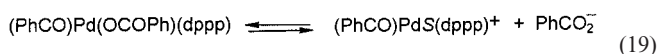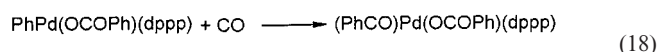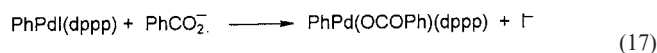trans-(PhCO)Pd(OCOPh)(PPh$_3$)$_2$ $\rightleftharpoons$ trans-(PhCO)PdS(PPh$_3$)$_2$$^+$ + PhCO$_2^-$

| + 1 dppp
| − 2 PPh$_3$

δ_4: 12.5 ppm (d, J_{PP} = 72 Hz) and δ_5: -7.9 ppm (d, J_{PP} = 72 Hz)
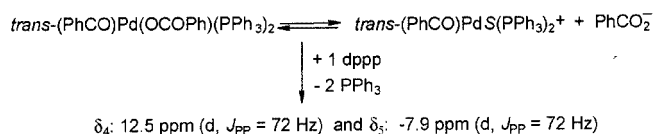
Scheme 1. Exchange of two PPh$_3$ ligands by one dppp in DMF

At least four complexes might be formed in DMF: [(PhCO)Pd(OCOPh)(dppp)], [(PhCO)PdS(dppp)]$^+$ and the complexes formed by decarbonylation {[PhPd(OCOPh)(dppp)] and/or [PhPdS(dppp)]$^+$}. The ^{31}P NMR signals of an authentic sample of [PhPdS(dppp)]$^+$[BF$_4$]$^-$ in DMF (two doublets at δ = 25.2 ppm and δ = −2.2 ppm, Table 2, entry 6) showed that such a complex was not formed in the exchange reaction of Scheme 1. When CO was bubbled into an NMR tube containing the authentic sample of the cationic complex [PhPdS(dppp)]$^+$[BF$_4$]$^-$ in DMF, two new broad doublets

were detected at δ = 5.1 and −8.4 ppm (Table 2, entry 7) and assigned to [(PhCO)PdS(dppp)$^+$] [Equation (16)].[24] Such a complex did not appear when PPh$_3$ was exchanged by dppp in Scheme 1.

PhPdS(dppp)$^+$ + CO $\longrightarrow$ (PhCO)PdS(dppp)$^+$

(16)
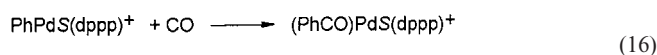
In order to discriminate between [(PhCO)Pd(OCOPh)(dppp)] and [PhPd(OCOPh)(dppp)], a series of experiments was then performed independently. To a solution of [PhPdI(PPh$_3$)$_2$] in DMF was first added one equiv. of dppp to generate [PhPdI(dppp)] characterized by two ^{31}P NMR doublets (δ = 12.4 ppm, $J_{P,P}$ = 53 Hz and δ = −8.6 ppm, $J_{P,P}$ = 53 Hz). Addition of 10 equiv. PhCO$_2^-$·Li$^+$ to the NMR tube resulted in the formation of a new complex assigned to [PhPd(OCOPh)(dppp)][21] (2 doublets at δ = 18.9 ppm and δ = −6.5 ppm, Table 2, entry 10) [Equation (17)]. This complex did not appear when PPh$_3$ was exchanged by dppp in Scheme 1.

PhPdI(dppp) + PhCO$_2^-$ $\longrightarrow$ PhPd(OCOPh)(dppp) + I$^-$

(17)

PhPd(OCOPh)(dppp) + CO $\longrightarrow$ (PhCO)Pd(OCOPh)(dppp)

(18)

(PhCO)Pd(OCOPh)(dppp) $\rightleftharpoons$ (PhCO)PdS(dppp)$^+$ + PhCO$_2^-$

(19)

When CO was bubbled into the NMR tube, the two doublets of [PhPd(OCOPh)(dppp)] disappeared, confirming the CO insertion [Equation (18)]. Two sets of two doublets were detected (relative integration of 1:4): a first set of two major doublets at δ_4 = 12.5 ppm and δ_5 = −7.9 ppm, assigned to [(PhCO)Pd(OCOPh)(dppp)] [Equation (18)] and already observed after the ligand exchange in Scheme 1, and a second set of two minor doublets at δ = 5.1 ppm and δ = −8.8 ppm (Table 2, entry 8) similar to [(PhCO)PdS(dppp)$^+$] previously characterized [vide supra, Table 2, entry 7, Equation (19)].

Consequently, the ligand exchange in Scheme 1 generated an acyl-Pd^{II} complex [(PhCO)Pd(OCOPh)(dppp)] but no phenyl-Pd^{II} complexes [PhPd(OCOPh)(dppp)] or [PhPdS(dppp)]$^+$ that would be formed by a decarbonylation process. The decarbonylation is definitively an endergonic process when phosphane ligands (monodentate or bidentate) are considered, which strongly stabilize neutral and cationic acyl-Pd^{II} complexes in DMF.

Conclusion

In DMF, the oxidative addition of benzoic anhydride to [Pd(PPh$_3$)$_4$] is slower than that of PhI but slightly faster than that of PhOTf and PhBr. This reaction gives two acyl-Pd^{II} complexes: the cationic complex trans-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ and the neutral complex trans-[(PhCO)Pd(OCOPh)(PPh$_3$)$_2$]. Aryl-Pd^{II} complex(es)

formed by decarbonylation of the two above acyl-Pd^{II} complexes have not been detected. Changing the monodentate PPh$_3$ ligand to the bidentate dppp does not favor the decarbonylation process either. This is why the Heck reaction, which requires the formation of an aryl-Pd^{II} complex, is much more efficient using catalytic Pd salts (in the absence of ligand) than catalytic phosphane-ligated Pd complexes when it is performed from benzoic anhydride.[2] The phosphane-ligated aryl-Pd^{II} complex must be present at very low concentration in an endergonic equilibrium with the major acyl-Pd^{II} complex(es) but be nevertheless more reactive with alkenes than the acyl-Pd^{II} complex(es). The decarbonylation of the acyl-Pd^{II} complex(es) ligated to the alkene, before the carbopalladation steps, appears more improbable.

Experimental Section

General Remarks: ^{31}P NMR spectra were recorded on a Bruker spectrometer (101 MHz) using H$_3$PO$_4$ as an external reference. Amperometry was performed with a generator Tacussel GSTP4. Conductivity was measured on a Radiometer Analytical CDM210 conductivity meter (cell constant: 1 cm^{-1}).

Chemicals: DMF was distilled from calcium hydride under vacuum. Commercial benzoic anhydride, phenyl triflate, PPh$_3$ and dppp (Acros) were used without any purification. [Pd(PPh$_3$)$_4$],[25] [PhPdBr(PPh$_3$)$_2$],[26] [PhPdI(PPh$_3$)$_2$],[26] and [PhPd(dppp)]$^+$[BF$_4$]$^-$ [27] were prepared according to described procedures.

Electrochemical Set-Up and Procedure for Kinetic Measurements: Experiments were carried out in a thermostatted 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 (Radiometer Analytical) separated from the solution by a bridge filled with 3 mL of DMF containing nBu$_4$N·BF$_4$ (0.3 M). The kinetic measurements were performed at a rotating gold disk electrode (Radiometer analytical, EDI 65109, diameter: 2 mm, angular velocity: 105 rad·s^{-1}) polarized at +0.35 V vs. SCE. [Pd(PPh$_3$)$_4$] (23.1 mg, 0.02 mmol) was introduced into 15 mL of DMF containing nBu$_4$N·BF$_4$ (0.3 mol dm^{-3}) followed by the appropriate amount of benzoic anhydride. The decay of the oxidation current was recorded as a function of time, up to 100% conversion.

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[12] Reductive elimination with formation of (PhCO)$_2$O would occur from a *cis*-[(PhCO)Pd(OCOPh)(PPh$_3$)$_2$] complex first formed in the oxidative addition before its isomerization to the *trans* complex, the final complex (see the second part of this work). Reductive elimination is usually inhibited by extra phosphanes, which favor the *cis/trans* isomerization. For a reductive elimination from [(PhCO)Pd(OCOPh)(PPh$_3$)$_2$] synthesized in situ by reacting CO with [PhPd(OCOPh)(PPh$_3$)$_2$] in the absence of extra phosphane, see ref.[9] and the comments on the deceleration of the reductive elimination due to the release of PPh$_3$ by decomposition of [Pd^0(PPh$_3$)$_2$] also generated in the course of the reductive elimination process. In the present work, free phosphanes were generated as the oxidative addition proceeded [Equation (7)]. Moreover, it seems that the reductive elimination is favored in the presence of CO for PPh$_3$ or PCy$_3$ ligands.[9]

[13] This situation has been observed in the oxidative addition of aryl triflates to [Pd(PPh$_3$)$_4$].[11]

[14] The kinetic treatment of the curve in Figure 2, featuring the kinetics of formation of the ionic species could not be done with high accuracy, since the value of the intrinsic conductivity κ$_{lim}$ of *trans*-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ could not be determined, due to the equilibrium (9) and to the "decomposition" process occurring at longer times. The first part of the curve ($t < 500$ s) featuring the kinetics of formation of the cationic complex *trans*-[(PhCO)PdS(PPh$_3$)$_2$]$^+$ was nevertheless analyzed after an estimation of κ$_{lim}$ = 110 μS·cm^{-1} and by neglecting the reverse reaction of equilibrium (9) over short time periods. The plot of ln((κ$_{lim}$ − κ)/κ$_{lim}$) *versus* time was not a straight line (κ: conductivity at t). The first linear part of the curve ($t < 100$ s) gives a value of k_{obs} = 0.0039 s^{-1}, not far from the value of k_{obs} = 0.0034 s^{-1} determined for the oxidative addition by amperometry (see a in Figure 1).

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[17] Acyl or arylcarboxy groups ligated to Pd^{II} complexes may be characterized by ^{31}P, ^{13}C NMR and IR spectroscopy.[6,7,9] However, our purpose was to investigate the structure of the complexes formed in the oxidative addition in the conditions of a Heck reaction, i.e., in solution in DMF. ^{13}C NMR spectroscopy cannot be performed in DMF. Moreover, since the oxidative addition was slow, a large excess of benzoic anhydride was required. The presence of DMF and benzoic anhydride in large amount excludes any characterization of the complexes formed in solution by IR spectroscopy.

[18] For a reaction of CO with cationic monoorgano-Pd^{II} complexes ligated by monodentate phosphanes, see ref.[8] and references therein.

[19] Cationic MeCO-Pd^{II} complexes formed by reaction of CO with the corresponding cationic Me-Pd^{II} complexes exhibit ^{31}P NMR signals at higher field than the starting complex, see: P. Braunstein, C. Frison, X. Morise, *Angew. Chem. Int. Ed.* **2000**, *39*, 2867−2870 and references therein.

[20] Grushin and Alper have reported that the ^{31}P NMR signal of [(PhCO)Pd(OCOPh)(PPh$_3$)$_2$] synthesized in situ by reacting CO with a [D$_6$]benzene solution of [PhPd(OCOPh)(PPh$_3$)$_2$] was

a singlet at δ = 18.3 ppm.[9] In our case (solvent: DMF containing 10% [D$_6$]acetone) the singlet of [(PhCO)Pd(OCOPh)(PPh$_3$)$_2$] was located at δ = 20.4 ppm. This difference is due to the solvent since we observed that the singlet of *trans*-[PhPd(OCOPh)(PPh$_3$)$_2$] at δ = 23 ppm in [D$_6$]benzene reported by Grushin and Alper[9] was located at δ = 21.6 ppm in DMF containing 10% [D$_6$]acetone (Table 2, entry 5).

[21] For the substitution of X by carboxylate anions in *trans*-[PhPdXL$_2$] (X = I, Br) see the reference given in ref.[15] and I. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, *60*, 7508−7510.

[22] Reaction of CO with monoorgano-Pd^{II} complexes to form acyl-Pd^{II} complexes has been widely developed and is reported to be faster with cationic complexes than with neutral complexes.[8,19]

[23] Grushin and Alper have reported the synthesis of [PhPd(OCOPh)(PPh$_3$)$_2$] by reacting [PhPd(μ-OCOPh)(PPh$_3$)]$_2$ with 2 PPh$_3$.[9] For its ^{31}P NMR characterization see the last part of the note in ref.[20].

[24] For reaction of CO with cationic monoorgano-Pd^{II} complexes ligated by bidentate phosphanes, see ref.[8] and G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, *Organometallics.* **1992**, *11*, 1598−1603.

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