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# Evidence of the Formation of Zerovalent Palladium from $Pd(OAc)_2$ and Triphenylphosphine

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The mixture $Pd(OAc)_2 + nPPh_3$ ($n \geq 2$) and the complex $Pd(OAc)_2(PPh_3)_2$ commonly used as catalysts in reactions involving aryl and vinyl halides, aryl triflates or allylic acetates spontaneously generate a zerovalent palladium complex that reacts with iodobenzene. Triphenylphosphine reduces the divalent palladium from the complex $Pd(OAc)_2(PPh_3)_2$ by an intramolecular reaction and is oxidized to triphenylphosphine oxide. In the presence of an excess of triphenylphosphine, the zerovalent palladium complex generated in situ has the same $^{31}P$ NMR and cyclic voltammetry properties as those of $Pd^0(PPh_3)_4$.

## Introduction

Most reactions involving aryl and vinyl halides, aryl triflates, and allylic acetates are catalyzed by zerovalent palladium complexes.[1] However in some cases, particularly in the Heck reaction (arylation or vinylation of olefins), the catalyst consists of the divalent complex $Pd(OAc)_2(PPh_3)_2$[2] or a mixture of a divalent palladium salt $Pd(OAc)_2$ with two[2a,b,d,3] or more than two[2c,3b,m,4] equivalents of a phosphine ligand usually $PPh_3$. Since divalent palladium complexes do not activate aryl or vinylic halides, aryl triflates, and allylic acetates, as zerovalent complexes do, there are many speculations on the origin of the zerovalent palladium complex which is able to activate these substrates, e.g., what is the reagent able to reduce the divalent palladium to zerovalent palladium: the olefin, the triphenylphosphine, the allylic acetate, etc.? We report therefore some evidence that triphenylphosphine can reduce $Pd(OAc)_2$ to a zerovalent palladium complex, using $^{31}P$ NMR and cyclic voltammetry as analytical techniques to detect and characterize the formation of zerovalent palladium complexes.

## Results

**I. Investigation of the System $Pd(OAc)_2 + 2PPh_3$.** A mixture of the brown solid $Pd(OAc)_2$, 2 mM, in THF (or DMF) with 2 equiv of triphenylphosphine $PPh_3$, first led to a yellow solution containing a complex that has been characterized by its reduction peak, $E^{\mathrm{p}}_{\mathrm{red}} = -1.38$ V vs SCE in THF (−1.18 V in DMF) (Figure 1a), similar to that of an authentic sample of $Pd(OAc)_2(PPh_3)_2$.[5]

$$Pd(OAc)_2 + 2PPh_3 \rightarrow Pd(OAc)_2(PPh_3)_2 \qquad (1)$$

We observed that this mixture was not stable and that it led spontaneously but slowly to a species detected by its oxidation peak, $E^{\mathrm{p}}_{\mathrm{ox}} = +0.255$ V in THF (+0.03 V in DMF) (Figure 1b). The oxidation peak current of this species increased with time concomitantly with a decrease of the reduction peak current of the divalent palladium complex $Pd(OAc)_2(PPh_3)_2$ (Figure 1a,b). Starting directly from the authentic complex $Pd(OAc)_2(PPh_3)_2$ resulted in the same evolution. After addition of iodobenzene, the oxidation peak was no more observed. This suggests that the species that is formed from spontaneous evolution of the complex $Pd(OAc)_2(PPh_3)_2$ is a zerovalent palladium complex $Pd^0(PPh_3)_n$ able to react with iodobenzene in an oxidative addition.[6]

$$Pd^{II}(OAc)_2(PPh_3)_2 \rightarrow\rightarrow \text{“}Pd^0(PPh_3)_n\text{”} + \text{products} \qquad (2)$$

$$\text{“}Pd^0(PPh_3)_n\text{”} + PhI \rightarrow Ph{-}Pd^{II}{-}I(PPh_3)_2 + (n-2)L \qquad (3)$$

Moreover the oxidation potential of this species is very similar to the oxidation potential of an authentic sample of $Pd^0(PPh_3)_4$, $E^{\mathrm{p}}_{\mathrm{ox}} = +0.262$ V in THF (+0.024 V in DMF), determined in the same experimental conditions, e.g. in the presence of acetate anions.[7] However, this

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(7) (a) In fact the oxidation peak of the in situ generated zerovalent palladium showed a shoulder at +0.13 V in THF. The electrochemical oxidation of $Pd^0(PPh_3)_4$ in THF, occurred at $E^{\mathrm{p}}_{\mathrm{ox}} = +0.359$ V with a shoulder at +0.262 V. These two oxidation peaks are respectively assigned to the oxidation of $Pd^0(PPh_3)_3(THF)$ and $Pd^0(PPh_3)_3$.[12] In the presence of 2 equiv of acetate anions (introduced as $nBu_4NOAc$), the zerovalent palladium complex was more easily oxidized, at +0.23 V with a shoulder at +0.106 V. In DMF, the in situ generated zerovalent palladium presented a single oxidation peak. The electrochemical oxidation of $Pd^0(PPh_3)_4$ in DMF also exhibited a single peak at $E^{\mathrm{p}}_{\mathrm{ox}} = +0.064$ V assigned to $Pd^0(PPh_3)_3(DMF)$.[12] In the presence of 2 equiv of acetate anions, the palladium complex was more easily oxidized, at +0.024 V. These results suggest that acetate anions can stabilize zerovalent palladium[7b] as chloride anions do.[9] (b) Amatore, C.; Jutand, A.; M'Barki, M. A. Unpublished results.

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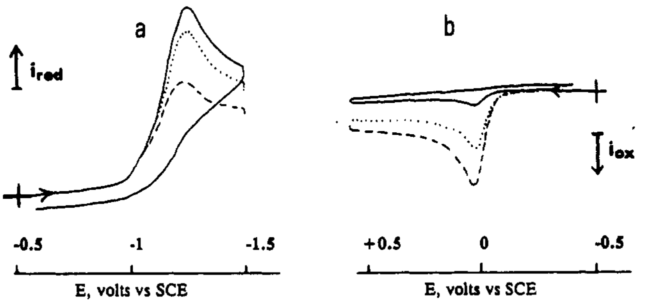

**Figure 1.** (a) Cyclic voltammetry of $Pd(OAc)_2$ (2 mM) and $PPh_3$ (4 mM) in DMF (0.3 M $nBu_4NBF_4$) at a stationary gold disk electrode (o.d. = 0.5 mm) with a scan rate of 0.2 $V{\cdot}s^{-1}$, from -0.5 to -1.5 V. The cyclic voltammetry has been performed as a function of time: (—) 4, (···) 14, (- - -) 33 min. (b) Cyclic voltammetry of the zerovalent palladium complex, generated in situ from $Pd(OAc)_2$ (2 mM) and $PPh_3$ (4 mM), in DMF (0.3 M $nBu_4NBF_4$) at the same electrode, with a scan rate of 0.2 $V{\cdot}s^{-1}$, from -0.5 to +0.5 V. The cyclic voltammetry has been performed as a function of time: (—) 7, (···) 17, (- - -) 31 min.

species was not very stable in the absence of any substrate and suddenly decomposed after 30 min before complete transformation of divalent palladium to zerovalent palladium, to give an orange solution in which no oxidation peaks could be detected. It is known that the complex $Pd^0(PPh_3)_4$ in solution in THF (or DMF) is mainly present as $Pd^0(PPh_3)_3$ with traces of the low-ligated $Pd^0(PPh_3)_2$[8] and that this solution is not stable in the absence of excess phosphines or halides.[9]

$$Pd^0(PPh_3)_4 \rightleftarrows Pd^0(PPh_3)_3 + PPh_3 \quad K_1 \gg 1 \qquad (4)$$

$$Pd^0(PPh_3)_3 \rightleftarrows Pd^0(PPh_3)_2 + PPh_3 \quad K_2 \ll 1 \qquad (5)$$

$$Pd^0(PPh_3)_2 \rightarrow ..... \qquad (6)$$

In the above report experiments in which only 2 equiv of triphenylphosphine per palladium were present, it is therefore easily understood why the in situ generated low-ligated zerovalent palladium was not stable. Attempt to characterize this species by $^{31}P$ NMR ($\delta$ vs $H_3PO_4$) led to spectra in which we could detect the characteristics signals of the triphenylphosphine oxide in THF at 24.38 ppm (25.47 ppm in DMF), $Pd(OAc)_2(PPh_3)_2$ at 14.48 ppm (15.08 in DMF),[10] and three signals at $\delta_1$ = 21.23, $\delta_2$ = 13.16, and $\delta_3$ = 12.67 ppm (respectively 21.20, 13.39, and 13.08 ppm in DMF). The characteristic signal of the free ligand at -0.525 ppm (-0.541 ppm in DMF) was not observed. Running $^{31}P$ NMR spectra as a function of time resulted in the growth of the signal of the triphenylphosphine oxide, of that of the signal at $\delta_1$, and to a larger extent of those at $\delta_2$ and $\delta_3$, at the expense of the signal of the divalent palladium $Pd(OAc)_2(PPh_3)_2$. Both signals $\delta_2$ and $\delta_3$ disappeared when iodobenzene was added to the NMR sample; they could then be reasonably assigned to zerovalent palladium complexes. Noteworthy, the signal at $\delta_1$ was still present. We could notice that the intensities of the two signals at $\delta_2$ and $\delta_3$ were always equal whatever the time, so they seem to characterize a single nonsymmetrical zerovalent palladium complex containing two chemically different triphenylphosphine ligands. The signal at $\delta_1$ could either represent a palladium complex that did not react with iodobenzene or a phosphorus derivative without palladium, viz. an intermediate leading to the formation of triphenylphosphine oxide (a phosphonium salt for example). In the absence of iodobenzene, the solution progressively decomposed and at least three new NMR signals could be detected but not assigned.

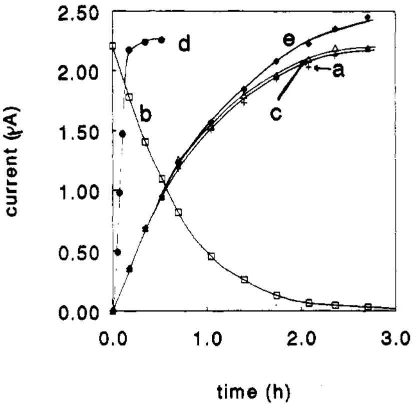

**Figure 2.** Variation of the plateau currents at a rotating gold disk electrode (o.d. = 2 mm; $\upsilon$ = 0.02 $V{\cdot}s^{-1}$; $\omega$ = 105 $rad{\cdot}s^{-1}$) of the system $Pd(OAc)_2$ (2 mM) and $PPh_3$ (20 mM) as a function of time: (a, +) Variation of the oxidation current in the in situ generated zerovalent palladium in DMF, at a potential of +0.4 V and at 25 °C; (b, □) variation of the reduction current of the divalent palladium complex in DMF, at a potential of -1.30 V and at 25 °C; (c, △) same conditions as in (a) but in THF; (d, ●) same conditions as in (a) but at 60 °C; (e, ◆) some conditions as in (a) but in the presence of $H_2O$ (20 mM).

At this point of the NMR and electrochemical studies, we could conclude that the systems $Pd(OAc)_2(PPh_3)_2$ or $Pd(OAc)_2$ + $2PPh_3$ slowly evolve to the formation of triphenylphosphine oxide and zerovalent palladium complex able to react with iodobenzene. Any attempt to isolate the zerovalent palladium complex failed; therefore, we decided to investigate the reaction in the presence of an excess of triphenylphosphine, so that any zerovalent palladium formed during the reaction could be stabilized.

**II. Investigation of the System $Pd(OAc)_2$ + $10PPh_3$.** In the presence of 10 equiv of triphenylphosphine the same phenomenon was observed; e.g., a slow formation of a zerovalent palladium complex detected by its oxidation peak at $E^p_{Ox}$ = +0.24 V in THF (+0.054 V in DMF)[7] with concomitant disappearance of the divalent palladium precursor complex. The reaction went to completion after 2 h (Figure 2), and the resulting zerovalent complex was stable in THF and DMF.

The $^{31}P$ NMR spectrum of this solution in THF exhibited only three signals, triphenylphosphine oxide at 24.42 ppm (25.46 ppm in DMF), $Pd(OAc)_2(PPh_3)_2$ at 14.42 ppm (15.14 ppm in DMF), and a signal at -4.70 ppm (-4.95 ppm in DMF) but no signal corresponding to free phosphine. Evolution as a function of time showed a growth of the triphenylphosphine oxide signal at the expense of that of $Pd(OAc)_2(PPh_3)_2$, while the signal at -4.70 ppm shifted gradually to lower field to -3.97 ppm (from -4.95 to -3.84 ppm in DMF). Addition of PhI to the NMR sample resulted in the disappearance of the signal at -3.97 ppm (-3.84 ppm in DMF) and formation of free triphenylphosphine at -5.25 ppm (-5.41 ppm in DMF). Beside the signal of $O{=}PPh_3$ we could observe new signals, one at 24.50 ppm (23,39 ppm in DMF) assigned to the insertion complex $Ph\text{-}Pd\text{-}I(PPh_3)_2$, by comparison with an authentic sample,[6] and a second one at 21.15 ppm (21.28 ppm in DMF) that was identical with the NMR signal obtained

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after addition of acetate anions to an authentic sample of Ph–Pd–$I(PPh_3)_2$:[11]

$$\underset{24.50\ \text{ppm}}{Ph\text{–}Pd\text{–}I(PPh_3)_2} + OAc^- \rightarrow \underset{21.15\ \text{ppm}}{Ph\text{–}Pd\text{–}OAc(PPh_3)_2} + I^- \quad (7)$$

Such an arylpalladium acetate intermediate has already been postulated.[2f]

These results yield evidence that the signal detected at −3.97 ppm (−3.84 ppm in DMF) characterizes a zerovalent palladium complex which reacts with iodobenzene to form the insertion complex with liberation of free phosphine. Moreover the $^{31}P$ NMR spectrum of an authentic sample of $Pd^0(PPh_3)_4$ in the presence of various amounts of triphenylphosphine similarly exhibited a unique signal with a chemical shift dependent on the excess of ligand.[12] The characteristic signal of $Pd^0(PPh_3)_4$ was a broad peak at +9 ppm which shifted to upper field and became thinner and thinner in the presence of excess ligand (5.48 ppm when 7 equiv of $PPh_3$ was added in DMF). We assign this unique signal to be the average signal of three species in fast equilibrium, $Pd^0(PPh_3)_3$, $Pd^0(PPh_3)_2$, and $PPh_3$ (eq 5).[12]

The great stability of the resulting zerovalent species allowed a kinetic investigation of this system, using steady-state cyclic voltammetry, performed at a rotating disk electrode, as the analytical technique.[13] The electrode was polarized at a potential (+0.4 V in THF and DMF) on the plateau of the oxidation wave of the zerovalent palladium, and the resulting current was recorded as a function of time. The same technique was used to monitor the disappearance of the starting divalent complex $Pd(OAc)_2(PPh_3)_2$ upon polarization on the plateau current of its reduction wave: −1.45 V in THF (−1.30 V in DMF). Figure 2 shows the formation of $Pd^0(PPh_3)_3$ at the expense of $Pd(OAc)_2(PPh_3)_2$. From curves a and b, we can conclude that the rate of formation of the zerovalent palladium and the rate of disappearance of the starting divalent palladium are identical. The rate of formation of the zerovalent palladium does not depend significantly on the solvent (compare curves a-DMF and c-THF), increases with temperature (curve d), and is not affected by the presence of additional water (curve e). We observed also that the rate of formation of the zerovalent palladium complex did not depend on the triphenylphosphine concentration. At the end of the reaction, addition of a known amount of an authentic sample of $Pd^0(PPh_3)_4$ resulted in an increase of the oxidation peak current of the in situ generated zerovalent complex and allowed the determination of the chemical yield of the zerovalent palladium complex which was found quantitative in THF and DMF. Cyclic voltammetry performed on the resulting solution exhibited the chemically reversible reduction peak of triphenylphosphine oxide at $E^p_{Red} = -2.61$ V (−2.50 V in DMF). However the proximity of this reduction peak with the reduction of the solvent did not allow the precise determination of the yield of $O{=}PPh_3$; yet the magnitude of its reduction peak was in agreement with an almost quantitative yield.

We could monitor the reactivity of the generated zerovalent palladium complex with iodobenzene by recording the variation of the plateau current of its oxidation wave as a function of time after addition of PhI.[8c,9] When the electrode was polarized at +0.4 V, the current first rapidly dropped to zero and then slowly increased to regain almost its initial value (Figure 3). The decreasing part of the curve represents the kinetics of the oxidative addition of iodobenzene with the zerovalent palladium.[8c,9] Since iodide anions are oxidized at +0.34 V, the increasing part of the curve may represent the kinetics of the slow substitution of the insertion complex Ph–Pd–$I(PPh_3)_2$ by a free acetate anion, affording free iodide, oxidized at the electrode (eq 7). This hypothesis was confirmed by the fact that when the electrode was polarized at +0.2 V, e.g. at a potential where iodides are not oxidized, the current dropped to zero and stabilized at this value.

## Discussion

It is clearly established from $^{31}P$ NMR spectroscopy and cyclic voltammetry that $Pd(OAc)_2$ in solution in THF or DMF first reacts with triphenylphosphine to form a complex $Pd(OAc)_2(PPh_3)_2$ which spontaneously evolves to give triphenylphosphine oxide and a zerovalent palladium complex, able to react with iodobenzene. In the presence of only 2 equiv of triphenylphosphine the resulting low-ligated zerovalent palladium is not stable as expected. Starting from the complex $Pd(OAc)_2(PPh_3)_2$ leads to the same conclusion. However, in the presence of excess phosphine ligand, a stable and well-defined zerovalent palladium complex has been detected and characterized by comparison with an authentic sample of $Pd^0(PPh_3)_4$. These results clearly establish that triphenylphosphine can reduce $Pd(OAc)_2$. The fact that a zerovalent palladium complex is formed from $Pd(OAc)_2(PPh_3)_2$ in the absence of triphenylphosphine and the fact that, in the presence of an excess of ligand, the kinetics of formation of the zerovalent palladium complex does not depend on the triphenylphosphine concentration suggest that the reduction step takes place from the complex $Pd(OAc)_2(PPh_3)_2$ by an intramolecular reaction. The role of the extra phosphine ligands is only to stabilize the resulting low-ligated zerovalent palladium. The reduction is quantitative.

While the complexes $PdX_2(PPh_3)_2$ (X = Cl, Br, I) are very stable in solution in THF (or DMF) and never evolve to the formation of zerovalent palladium,[9] it is reported that triphenylphosphine can reduce palladium oxide PdO or the divalent nitrate complex $Pd(NO_3)_2$ in the presence of excess ligand, to afford $Pd^0(PPh_3)_4$ together with $O{=}PPh_3$ and $N_2O$.[14] The authors claimed that the oxygen of the triphenylphosphine oxide came from the ligand $NO_3$. It seems that the reduction of divalent palladium to zerovalent palladium only occurs when the divalent palladium is associated with an oxygenated ligand, $NO_3^-$, $AcO^-$, or oxide. In the case of $Pd(OAc)_2$, up to now, the origin of the oxygen of the triphenylphosphine oxide is not clear. We know that a free ligand $AcO^-$ is present in solution since, in the presence of iodobenzene, we could observe the reaction of the acetate anion with the insertion complex (eq 7), but no characterization of the other acetate ligand as free acetate (which could have been detected by its oxidation peak, $E^p_{Ox} = +0.9$ V in THF) or other derivatives has been possible.

The presence of water did not affect the rate of the formation of the zerovalent palladium. That means that if residual water is involved in the mechanism of the formation of zerovalent palladium, this reaction takes place after the rate-determining step of the reaction, which is

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[11] A third signal was detected at 21.41 ppm in THF (21.79 ppm in DMF) which has not been assigned.

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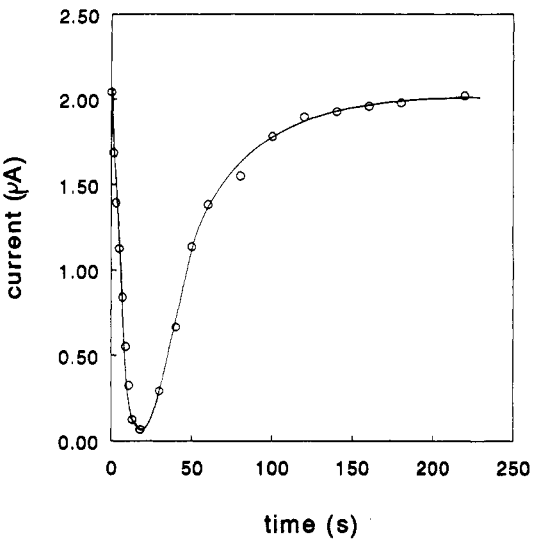
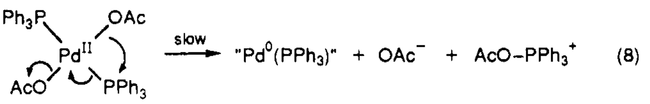


**Figure 3.** Variation of the oxidation plateau current at +0.4 V, at a rotating gold disk electrode (o.d. = 2 min; $v$ = 0.02 V·s$^{-1}$; $\omega$ = 105 rad·s$^{-1}$), of the zerovalent palladium complex (generated quantitatively from $Pd(OAc)_2$ (20 mM) and $PPh_3$ (20 mM) after 3 h; Figure 2, curve a) in the presence of iodobenzene (20 mM) as a function of time in DMF at 25 °C.

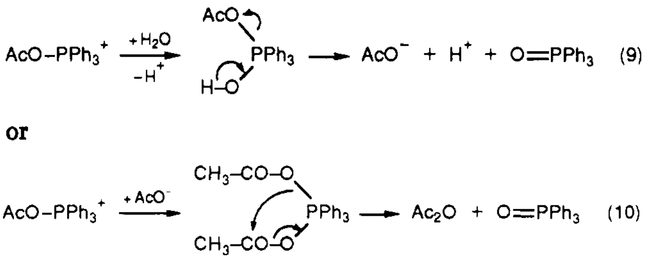
the intramolecular reduction step.

A tentative explanation for the reduction of $Pd(OAc)_2$, by triphenylphosphine can be summarized in the following scheme:

$$\mathrm{Pd(OAc)_2 + 2PPh_3 \xrightarrow{fast} Pd(OAc)_2(PPh_3)_2} \qquad (1)$$



This latter reaction, a kind of reductive elimination, may be followed by fast steps leading to triphenylphosphine oxide as e.g.



$$\mathrm{"Pd^0(PPh_3)" + 2PPh_3 \xrightarrow{fast} Pd^0(PPh_3)_3} \qquad (11)$$

The species "$Pd^0(PPh_3)$" can only be detected from the complex $Pd(OAc)_2(PPh_3)_2$ in the absence of triphenylphosphine. In the $^{31}$P NMR spectrum of this system, the zerovalent palladium complex that reacted with iodobenzene has been characterized by the two equal signals at $\delta_2$ and $\delta_3$, characterizing two different triphenylphosphine ligands. This low-ligated complex is certainly a dimer $[Pd^0{}_2(PPh_3)_2(OAc)_xS_y]^{x-}$, with solvent and acetate anions as ligands.[7] Its structure could not be further investigated because of its instability.

## Conclusion

The mixture $Pd(OAc)_2$ and $nPPh_3$ ($n \geq 2$) or $Pd(OAc)_2(PPh_3)_2$, which are commonly used as catalysts in reactions involving aryl and vinyl halides, aryl triflates, or allylic acetates, generates in situ a zerovalent palladium complex. Triphenylphosphine can reduce divalent palladium diacetate to zerovalent palladium and is oxidized to triphenylphosphine oxide. The reduction certainly consists in an intramolecular reaction from the complex $Pd(OAc)_2(PPh_3)_2$. In the presence of only two ligands, a low-ligated unstable complex is formed which can be trapped by iodobenzene by an oxidative addition. The stable complex which is generated in the presence of excess triphenylphosphine has the same $^{31}$P NMR and electrochemical properties as the tetrakis(triphenylphosphine) complex $Pd^0(PPh_3)_4$ placed under identical conditions. The origin of the oxygen of the triphenylphosphine oxide is still under investigation.

## Experimental Section

$^{31}$P NMR spectra were recorded on a Bruker spectrometer (162 MHz) using $H_3PO_4$ as an internal reference. All the experiments were performed at 25 °C under argon.

**Chemicals.** THF was dried on potassium hydroxide and distilled from sodium benzophenone. DMF was distilled from calcium hydride. Iodobenzene was commercial and used after filtration on alumina. $Pd(OAc)_2$ and triphenylphosphine were from a commercial source (Janssen). Authentic samples of $Pd(OAc)_2(PPh_3)_2$,[5] $PhPdI(PPh_3)_2$,[6] and $Pd^0(PPh_3)_4$[15] were prepared according to described procedures. $nBu_4NBF_4$ was obtained from the tetrabutylammonium hydrogen sulfate salt (Janssen) by treatment with $NaBF_4$ (Janssen) in water. The precipitate was recrystallized from ethyl acetate and petroleum ether, dried under vacuum, and stored under argon before use. $nBu_4NOAc$ was synthesized by treatment of the tetrabutylammonium hydrogen sulfate salt (Janssen) with NaOAc (Janssen) in water. Extraction of the tetrabutylammonium acetate salt by dichloromethane and evaporation of the solvent afforded a white solid, mp = 117 °C (Lit[16] mp = 118 °C).

**Electrochemical Setup and Electrochemical Procedure for Cyclic Voltammetry.** Cyclic voltammetry was performed with a homemade potentiostat[17] and a wave-form generator, PAR Model 175. The cyclic voltammograms were recorded with a Nicolet 3091 digital oscilloscope. Experiments were carried out in a three-electrode cell connected to a Schlenk line. The counter electrode was a platinum wire of ca. 1-cm$^2$ apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge (3 mL) filled with a 0.3 M $nBu_4NBF_4$ solution in THF (or DMF). A 12-mL volume of THF (or DMF) containing 0.3 M $nBu_4NBF_4$ was poured into the cell. A 5.4-mg amount ($2 \times 10^{-3}$ M) of $Pd(OAc)_2$ was then added, followed by 12.6 mg ($4 \times 10^{-3}$ M) or 63 mg ($20 \times 10^{-3}$ M) of triphenylphosphine. The cyclic voltammetry was performed at a stationary disk electrode (a gold disk made from cross section of wire (o.d. = 0.5 mm) sealed into glass) with a scan rate of 0.2 V·s$^{-1}$.

The kinetic measurements were performed by steady-state cyclic voltammetry at a rotating disk electrode (a gold disk (o.d. 2 mm) inserted into a Teflon holder, Tacussel EDI 65109) with a scan rate of 0.02 V·s$^{-1}$ and an angular velocity of 105 rad·s$^{-1}$ (Tacussel controvit). The RDE was polarized on the plateau of the reduction wave of the bivalent palladium complex, and the reduction current was monitored as a function of time up to 100% conversion. In another set of experiments, the RDE was polarized on the plateau of the oxidation wave of the zerovalent palladium complex, and the oxidation current was monitored as a function of time. When the limit of the oxidation current was reached, 10 equiv of iodobenzene was added to the cell, and the oxidation current was recorded to follow the kinetics of oxidative addition of PhI[8c,9] and then the kinetics of the iodide substitution in the insertion complex $PhPd(PPh_3)_2$ by acetate anions.

For $^{31}$P NMR studies, an NMR tube filled with argon and equipped with a septum was filled with the solution to be analyzed,

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by using a cannula according to standard Schlenk procedure.

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**Registry No.** $Pd(OAc)_2(PPh_3)_2$, 14588-08-0; $Pd(PPh_3)_2$, 31989-57-8; $PhPd^{II}I(PPh_3)_2$, 55123-60-9; $Pd(PPh_3)_4$, 14221-01-3; $POPh_3$, 791-28-6; $PhPdOAc(PPh_3)_2$, 56925-72-5; $Pd(PPh_3)_3$, 28516-49-6.

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# Cyclometalation of *N*-(4-Methoxyphenyl)-$\alpha$-benzoylbenzylideneamine with Palladium(II) Acetate. Evidence for a New Kind of Diastereoisomerism

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The reaction of $Pd(OAc)_2$ with *N*-(4-methoxyphenyl)-$\alpha$-benzoylbenzylideneamine yielded two different acetate-bridged ortho-palladated compounds, $Pd_2[4\text{-}OCH_3C_6H_4N{=}C(COC_6H_5)C_6H_5]_2(\mu\text{-}OAc)_2$ (**2** and **3**), depending on the relative ratio of the reagents. Both diastereoisomeric complexes exhibit a nonplanar, open-book shape, differing only in the dihedral angle formed between the $C_6H_5C{=}O$ and the $C_6H_5C{=}N$ planes; i.e., they are atropisomers around the CO–CN bond, as could be established from X-ray diffraction data. Both complexes crystallize in the centrosymmetric triclinic space group $P\bar{1}$, with $Z = 2$. Unit cell parameters are as follows: compound **2**, $a = 14.206$ (9) Å, $b = 15.764$ (5) Å, $c = 11.149$ (3) Å, $\alpha = 92.46$ (2)°, $\beta = 95.31$ (4)°, $\gamma = 116.03$ (4)°; compound **3**, $a = 11.889$ (15) Å, $b = 13.209$ (23) Å, $c = 15.436$ (9) Å, $\alpha = 87.34$ (1)°, $\beta = 78.51$ (7)°, $\gamma = 87.73$ (1)°.

## Introduction

The ortho-palladation reaction of benzylamines and related derivatives is a well-known process. Also, the characteristic form of the complexes resulting from these reactions is known.[1] Of special interest are those dimers containing two palladium centers linked by two bridging acetate groups. In these cases, the acetate groups can force the two square planes of each palladium atom to have a relatively small dihedral angle,[2] resulting in the molecule adopting a nonplanar open-book shape. This configuration does not undergo inversion under literature conditions[3] (opposite to the fluxionality observed in other complexes exhibiting an open-book structure in the solid state[4]), and therefore, the complexes are chiral. This new kind of chirality has been postulated from NMR studies on carboxylato-bridged ortho-palladated azines containing a chiral center at the carboxylated moiety.[5]

The benzoylbenzylideneamines prepared from chiral nonracemic amines exhibit mutarotation in several solvents.[6] This fact was explained by assuming an equilibrium between the atropisomers A and B (Figure 1), resulting from the restricted rotation around the CO–CN bond, which becomes a chiral axis. Nevertheless, this proposal, which was based on kinetic considerations,[7] was never unequivocally demonstrated because of the inability to isolate each atropisomer, probably due to the low activation energy for rotation.

The interest in these compounds as ligands derives from the different adducts which can be formed, depending on the size of the cyclometalated ring,[8] the nature of the heteroatom involved (oxygen or nitrogen), or the stereochemistry (cis or trans) adopted for the two imine molecules involved in the dinuclear species which must presumably be formed. There is another factor related to the open-book shape of the complexes, which suggests the possibility of increasing the activation energy for rotation around the CO–CN bond sufficiently, to allow the isolation of the atropisomers, which would afford unambiguous evidence for both chiral axes (the CO–CN bond and the spine of the book).

We herein report the synthesis, spectroscopic characterization, and X-ray diffraction data for the two atropisomeric complexes resulting from the reactions of Pd(O-

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