Providing Support in Favor of the Existence of a Pd^{II}/Pd^{IV} Catalytic Cycle in a Heck-Type Reaction

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Abstract: The complex [Pd(O,N,C-L)(OAc)], where L is a monoanionic pincer ligand derived from 2,6-diacetylpyridine, reacts with IBzOH at room temperature to afford the very stable pair of Pd^{IV} complexes (OC-6-54)- and (OC-6-26)-[Pd(O,N,C-L)(O,C-C$_6$H$_4$CO$_2$-2)I] (1.5:1 molar ratio, at –55 ºC). These complexes and the Pd^{II} species [Pd(*O,N,C*-L)(OX)] and [Pd(*O,N,C*-L')(NCMe)]ClO$_4$, (X = MeC(O) or ClO$_3$, L' = another monoanionic pincer ligand derived from 2,6-diacetylpyridine), are precatalysts for the arylation of CH$_2$=CHR (R = CO$_2$Me, CO$_2$Et, Ph) using IC$_6$H$_4$CO$_2$H-2 and AgClO$_4$. These catalytic reactions have been studied and a tentative mechanism is proposed. The presence of two Pd^{IV} complexes is detected by ESI(+)-MS during the catalytic process. All data obtained strongly support a Pd^{II}/Pd^{IV} catalytic cycle.

Introduction

The recent award of the 2010 Nobel Prize in Chemistry to Heck, Negishi and Suzuki for their studies on catalytic cross couplings has recognized the important role of palladium in organic synthesis.[1,2] These reactions, and most of those using Herrmann's palladacycles as precatalysts,[3] involve an aryl halide and a Pd(0) catalyst[4,5] which forms from Pd(0)[1] or Pd^{II} precatalysts.[6-14] However, based on experimental data[15-17] and computational studies,[8,18] Pd^{II}/Pd^{IV} cycles have been proposed when using Pd^{II} precatalysts.[19] The present relevance, topicality and interest of this proposal has been covered and emphasized in many papers.[4,7,8,16,18-22] They insist on the need for experiments addressed to detect some aryl-Pd^{IV} species in those catalytic reactions in which the intermediacy of Pd(0) complexes or Pd nanoparticles has been ruled out. We believe that this has become one of the most intriguing open problems in homogeneous catalysis. Additionally, the use of oxidizing agents stronger than aryl halides (for example, iodonium salts, peroxo-compounds, O_2) to form Pd^{IV} catalysts from Pd^{II} precatalysts is at present one emerging research area of interest in organic synthesis.[16,20,23] Although these oxidation reactions are well documented, experimental evidence of the presence of Pd^{IV} species in catalytic cycles has neither been provided so far. The involvement of a bimetallic Pd(III) complex in palladium-catalyzed carbon-heteroatom formation has been proved.[21]

Of course, the elusive nature of intermediates in a catalytic cycle is behind the difficulty in proving their presence in the reaction mixture, for example, by using NMR spectroscopy. Fortunately, electrospray ionization mass spectrometry (ESI-MS) is especially useful in detecting ions without destroying molecules. It allows even short-lived intermediates to be captured from the reaction solution to the gas phase.[24] It is so mild that viral material can remain viable after an electrospray ionization process.[25] Being, in addition, a fast and high-sensitivity technique it can provide accurate information of the ions present in reaction solutions, allowing their capture and characterization, thus facilitating mechanistic

studies.[26] In particular, it has been reported that "observation of complexes under catalytic conditions by ESI-MS indicates that they are intermediates in the reaction".[27] The important applications of this technique in studying macromolecules earned John B. Fenn the 2002 Nobel Prize in Chemistry.[28]

Another weak point of the Pd^{II}/Pd^{IV} catalytic cycle proposal was that the required oxidative addition of an aryl halide to a Pd^{II} complex had not been proved.[14] However, we recently communicated the isolation of $[Pd(O,N,C\text{-}L)(C,O\text{-}C_6H_4CO_2\text{-}2)I]$ (**1**, Scheme 1) from the reaction of $[Pd(O,N,C\text{-}L)(OAc)]$ (**2·OAc**) with IBzOH (IBzOH).[29] ^1H NMR studies showed that **1** exists as an equilibrium mixture of two isomers and that they are also in equilibrium with its Pd^{II} precursor $[Pd(O,N,C\text{-}L)(O_2CC_6H_4I\text{-}2)]$ (**2·OBzI**). Finally, we reported (1) that **1** is a precatalyst for the synthesis of (*E*)-methyl 2-carboxycinnamate (**3a**, Scheme 2) from $CH_2=CHCO_2Me$ and IBzOH, in the presence of one equiv of $AgClO_4$ and (2) that the addition to the catalytic reaction of Hg (4000 equiv per Pd) or benzyl chloride (5 equiv/Pd)[30] neither quenched the process nor afforded dibenzyl, respectively, thus excluding the involvement of Pd nanoparticles (see below) [9,12,17] or some Pd(0) complex, respectively, as the catalyst in the reaction.[8] These data suggested that Pd^{II}/Pd^{IV} species could be involved in the catalytic cycle.

In spite of the above results, it needs to be taken into account that although the Pd^{IV} complex **1** is a precatalyst, this does not mean that it is involved in the catalytic cycle. Therefore, we found it essential to go some steps further, by studying the catalytic reaction using NMR spectroscopy and ESI-MS to obtain kinetic data and information on species present in solution, particularly some aryl-Pd^{IV} complex, which is our main objective. In addition, these studies could help us to propose a mechanism or to detect some Pd^{II} complex that we could synthesize to use it as precatalyst. This is indispensable because the use of a Pd^{IV} complex as precatalyst (as we did using **1** in our communication)[29] could introduce reasonable doubts as to whether any detected signal of a Pd^{IV} complex could be

attributed to the added Pd^{IV} complex or some derivative not intervening in the catalytic cycle.

Scheme 1. Synthesis of aryl Pd(IV) complexes by an oxidative addition reaction.

Results and Discussion

Complex **1** is also a precatalyst for the synthesis of other arylated olefins such as **3b** and **3c** (Scheme 2). The Heck syntheses of these products, using the aryldiazonium salt instead of IBzOH, have been reported.[31] As expected, complex **1** can be replaced by its precursor **2·OAc** in the catalytic reaction.

   The beginning of the catalytic reaction. Use of the Pd^{II} complex [Pd(*O,N,C*-L)(OClO₃)] (2·OClO₃) as precatalyst. Using **1** as precatalyst at room temperature in the synthesis of **3a** (from now on "the reaction"), we initially detected only a Pd^{II} pincer-complex by ^1H NMR, which we assumed to be the solvento complex [Pd(*O,N,C*-L)S]ClO₄ ([**2·S**]ClO₄, S = [D₆]acetone, Scheme 2) because (1) it shows the CH_2 ^1H NMR resonance at 3.49 ppm, which is similar to that observed in [Pd(*O,N,C*-L)X] (in ppm: X = Cl (**2·Cl**; Scheme 1), 3.52; Br, 3.50, I, 3.49; OAc, 3.54; $O_2CC_6H_4Br$-2 (**2·OBzBr**), 3.66) but more shielded than that in the related Pd^{IV} derivatives [Pd(*O,N,C*-L)X₃] (in ppm: X = Cl, 6.03; Br, 6.04; I, 6.29 and 6.01) and **1**, 4.95, 4.55 ppm),[29,32,33] (2) we have prepared solutions of

[**2**·S]ClO$_4$ (2a) by dissolving in acetone [Pd(*O,N,C*-L)(OClO$_3$)] (**2**·OClO$_3$), which was

isolated by reacting **2**·Cl (Scheme 1)[32] with one equiv of AgClO$_4$ and behaves in acetone

as an 1:1 electrolyte (Λ_M = 81 $\wedge$·cm^2·mol^{-1}),[34] and (2b) from the stoichiometric reactions **1**

+ CH$_2$=CHR (R = CO$_2$Me, CO$_2$Et, Ph) + AgClO$_4$ + S → [**2**·S]ClO$_4$ + **3** + AgI (Scheme 2)

and (3) **2**·OClO$_3$ behaves as a precatalyst for the reaction (quantitative yield of **3a** in 40

min).
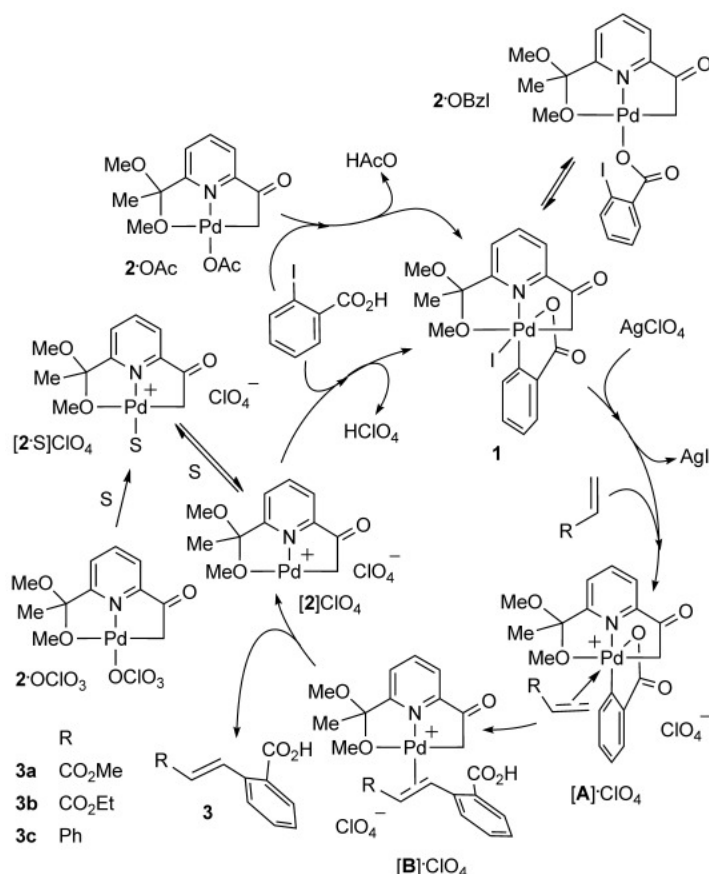
Scheme 2. Proposed catalytic cycle for the synthesis of 2-vinyl benzoic acids involving

precatalysts 1, **2**·OAc, or **2**·OClO$_3$.

The evolution and the end of the reaction. **The new Pd^{II} complex [Pd(*O,N,C*-**

L')(NCMe)]ClO$_4$ ([2'·NCMe]ClO$_4$) can be used as precatalyst. Following the course of

the reaction, a decrease of the amount of [**2**·S]ClO$_4$ with time was observed while MeOH

and a new Pd^{II} complex appeared. Its ^{1}H NMR spectrum showed ^{TM}(CH$_2$) at 3.65 ppm,

suggesting it is [Pd(*O,N,C*-L')S]ClO$_4$ ([**2'**·S]ClO$_4$; Scheme 3) resulting from the

hydrolysis of [**2**·S]ClO$_4$,[29,32,33] where L' is the monoanionic ligand resulting from monodeprotonation of one acetyl group of 2,6-diacetylpyridine. The presence of water (from the non-anhydrous acetone or the atmosphere) and the acidic medium (IBzOH and HClO$_4$; Scheme 2) must be responsible for this acid-catalyzed hydrolytic process.

The proposed nature of [**2'**·S]ClO$_4$ was confirmed by concentrating a solution of the catalytic reaction, adding MeCN and then precipitating with Et$_2$O its homologue [**2'**·NCMe]ClO$_4$ (Scheme 3). Its ^{1}H NMR spectrum in [D$_6$]acetone shows resonances of the pincer ligand at chemical shifts almost identical to those of [**2'**·S]ClO$_4$ ($\pm$ 0.05 ppm), suggesting that replacement of MeCN by acetone occurs in solution to give [**2'**·S]ClO$_4$. Correspondingly, [**2'**·NCMe]ClO$_4$ is also a precatalyst for the catalytic reaction. [**2'**·S]ClO$_4$ was detected in amounts increasing with time in all catalytic reactions using **1**, **2**·OAc or **2**·OClO$_3$ as precatalysts, while the amount of [**2**·S]ClO$_4$, decreased until its total disappearance. This means that two catalytic cycles can operate simultaneously while [**2**·S]ClO$_4$ and [**2'**·S]ClO$_4$ coexist (Schemes 2 and 3).

Conversion *vs.* time plots. Figure 1 shows conversion (%) *vs.* time (min) plots for the synthesis of **3a** using the **1**, **2**·OAc or [**2'**·NCMe]ClO$_4$ precatalysts (from now "the three precatalysts"). The data show that the reaction rate decreases in the order [**2'**·NCMe]ClO$_4$ > **2**·OAc > **1** (See "[**2'**·NCMe]ClO$_4$", "**2**·OAc" and "**1**" plots in Figure 1). A ^{1}H NMR study of the catalytic reaction mixture using **2**·OAc or **1** showed almost immediate formation of complex [**2**·S]ClO$_4$ while [**2'**·S]ClO$_4$ appeared later in the catalytic reaction from **1** (40% after 30 min) than in that from **2**·OAc (90% in 20 min). This explains that the reaction rate is greater from **2**·OAc that from **1**; in other words, the sooner the best precatalyst [**2'**·S]ClO$_4$ forms, the faster the reaction goes. The faster formation of [**2'**·S]ClO$_4$ from **2**·OAc than from **1** is surprising because **1** forms from **2**·OAc. This could be explained if **2**·OAc, or some intermediate in the reaction **2**·OAc $\rightarrow$ **1**, hydrolyzed faster than **1** to afford [**2'**·S]ClO$_4$.
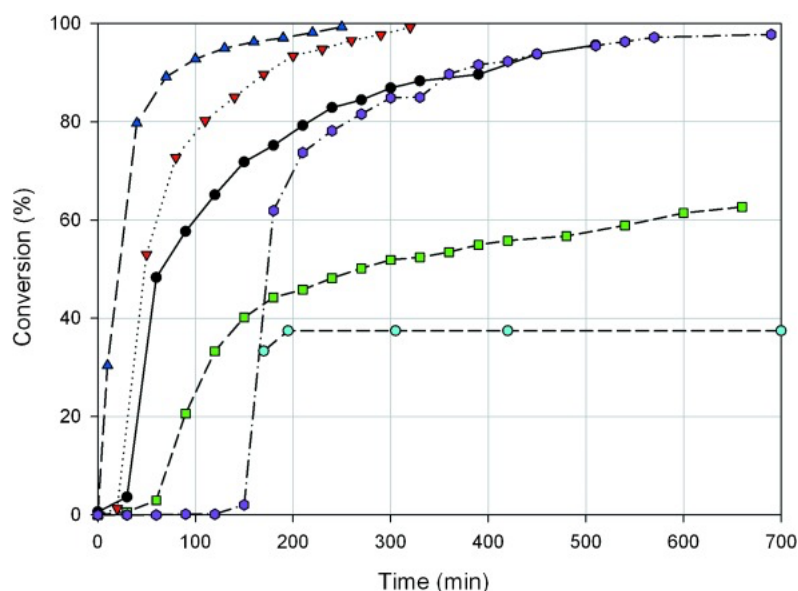
Figure 1.

Homogeneous or heterogeneous catalysis? We have checked that Pd nanoparticles are not involved in the catalytic cycle when using any of the three precatalysts. In fact, Hg addition (4000 equiv of Hg per Pd) did not quench the catalytic reaction[6-8,10,35] although reduced its rate. The same behavior has been previously reported in Heck-type reactions using an homogenous catalyst.[9,36] This is likely attributable to a decrease in the concentration of some intermediate in the catalytic cycle. In fact, a marked rate decrease when using 1% instead of 10% of precatalyst **2**·OAc was observed (compare plots "**2**·OAc" and "**2**·OAc (1%)" in Figure 1). This behavior also differs from that of reactions catalyzed by nanoparticles that usually utilize less than 0,1% of catalyst. In some cases at higher concentrations, palladium black forms and the reaction stops.[37] The reaction using **2**·OAc as precatalyst was neither quenched upon the addition of any of the poisoning agents CS_2, PPh_3 or thiophene, in amounts of 0.5–1 equiv/Pd.[10]
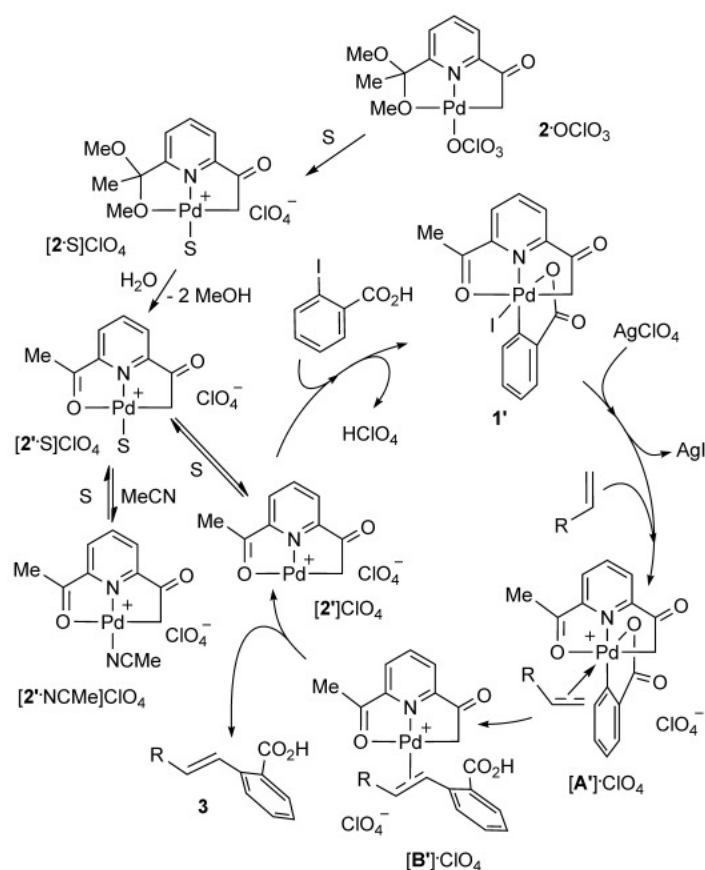
Scheme 3.

We have also considered the possibility that the catalyst were small size soluble Pd

nanoparticles (soluble metal clusters). However, as we did not find a test to detect them, we

repeated a reported catalytic reaction using such type of nanoparticles[38] in the presence of

Hg (300 eq per Pd). The quenching of this reaction means that the Hg test is valid for both

types of nanoparticles. Therefore, our reaction does not involve nanoparticles (soluble or

not) as catalysts.

The involvement of some soluble Pd(0) complex was also ruled out because using any

of the three precatalysts and 5 equiv/Pd of benzyl chloride in the catalytic reaction gave

98%, 80% (5 h at room temperature) or 97% (3 h at room temperature) yield of **3a**,

respectively, while dibenzyl was not detected.[8] In addition, the reaction is carried out

under atmospheric conditions, while most Pd(0) catalyzed C–C coupling reactions require a

protected atmosphere.

The homogeneous nature of the reaction when any of the three precatalysts is used is also supported by the very short induction period (Figure 1), the data reproducibility, and the striking dependence of the rate on the concentration of the precatalyst.[9,35,37]

The catalytic reaction using **2**·OAc, changed to heterogeneous when AgTfO was used instead AgClO$_4$ (compare plots "**2**·OAc" and "**2**·OAc+AgTfO" in Figure 1). In this case, no reaction was observed after 8h at room temperature when 4000 equiv of Hg/Pd were added to the initial mixture. When the same amount of Hg was added after 3 h of catalytic activity, the conversion was instantly quelled (compare plots "**2**·OAc+AgTfO" and "**2**·OAc+AgTfO+Hg" in Figure 1). The long induction period for this reaction shows (1) its heterogeneous nature[7,8,10,11,35] and (2) the difference with respect to those using any of the three precatalysts. In an attempt to isolate [Pd(O,N,C-L)(OTf)] (**2**·OTf), we reacted **2**·OAc[29] with one equiv of HTfO in [D$_6$]acetone at room temperature; however, the resulting product started to decompose after 30 min and finished after approx 5h giving a mixture in which we observed the formation of Pd metal and identified (HL)TfO only. The corresponding salts, (HL)ClO$_4$ or (HL')ClO$_4$, were never detected when any of the three precatalysts were used, which suggests the exclusive involvement of the pincer complexes in the catalytic cycle. The inability of **2**·OTf during its lifetime to act as a homogeneous catalyst could be attributed to the Pd–OTf bond being stronger than that in Pd–OClO$_3$ or Pd–OCMe$_2$. This could preclude (1) the coordination of the OBzI$^-$ anion to give **2**·OBzI and, correspondingly, the oxidative addition to afford **1** or (2) the necessary coordination of the olefin. We have reported that the catalyst in the reaction at high temperatures (typical Heck conditions), using **1** as precatalyst in the absence of AgClO$_4$, is Pd in the form of nanoparticles.[29]

All the above tests and observations show that our reaction is neither heterogeneous nor homogeneous through soluble Pd clusters, ligand-free or ligand-containing Pd(0) species.

Looking for intermediates in the catalytic reaction by use of ESI(+)-MS. The above conclusion suggests that the catalysis takes place by oxidizing a Pd[II] complex with IBzOH. It has recently been reported that a dinuclear Pd[III] complex bearing two acetato bridging ligands is a catalyst in the reaction of benzo[h]quinoline with PhICl$_2$ or *N*-chlorosuccinimide to afford 10-chlorobenzo[h]quinoline.[21] Although **2·OAc** is a dinuclear complex of the type required for this kind of catalysis, it is monomeric in solution and we have shown its reaction with IBzOH not to give a dinuclear species but the mononuclear aryl-Pd[IV] complex **1**.[29] In the case of the other Pd[II] precatalysts [**2·S**]ClO$_4$ or [**2'·S**]ClO$_4$ formation of Pd[III] complexes using IBzOH as oxidant is very unlikely.

One electron oxidation of a Pd[II] complex using a ferrocinium or a Ag$^+$ salt has been reported as an intermediate step in a stoichiometric reductive elimination reaction.[39] In our case, oxidation of some Pd[II] complex by Ag$^+$ to give a Pd[III] (or Pd[IV]) complex can be ruled out because a ^{1}H NMR study shows that the reaction **2·**OClO$_3$ + AgClO$_4$ + IBzOH does not take place unless the olefin is added. In addition, we have discarded the involvement of AgClO$_4$ and/or AgI in the catalytic reactions after confirming, by ^{1}H NMR in [D$_6$]acetone, that the reaction IBzOH + 0.5 AgI + 0.5 AgClO$_4$ + 0.5 HClO$_4$ + 2 CH$_2$=CHCO$_2$Me does not take place.

Trying to establish if **1** can be obtained from **2·**OClO$_3$, as suggested in Scheme 2, the ESI(+)-MS of a 1:10 mixture of **2·**OClO$_3$ and IBzOH was measured in acetone with 1% MeCN, to intercept species with this ligand, and 1 mmol/L aq solution of HClO$_4$ (0.3 equiv/IBzOH), to mimic the acidic conditions in the catalytic reaction. The peaks intercepted around 342 and 355 m/z (see supporting information, SI) correspond to the Pd[II] adducts [**2·**N$_2$]$^+$,[40] and [**2·**NCMe]$^+$ (both also detected by ESI(+)-MS in a solution of **2·**OClO$_3$). Those around 562 m/z can only be assigned to the Pd[II] [**2·**OBzI+H$^+$] and Pd[IV] [**1**+H$^+$] isomers (mean error for the 5 more intense peaks of the three groups of signals is 0.3 ppm), which parent neutral species we have reported to be in a slow equilibrium with

each other (Schemes 1 and 2).[29] About the ratio [**1**+H$^+$]:[**2**·OBzI+H$^+$] in solution, it is realistic to assume that it is much greater than that between the unprotonated species (2.3:1 at 25 ºC), because IBzOH (*i.e.*, IBzO$^-$+H$^+$) must be a poor donor easily replaceable by acetone or MeCN contributing to the peaks at 342 and 355 m/z. In short, the concentration of the benzoato complex **2**·OBzI in a strong acid medium (HClO$_4$) must be very low or even zero. Contrarily, in [**1**+H$^+$] the ligand 2-C$_6$H$_4$CO$_2$H (i.e., 2-C$_6$H$_4$CO$_2^-$+H$^+$) is expected to act as *C,O*-chelating, with a very strong Pd–C bond. An experimental support of the very low or null concentration of **2**·OBzI in the presence of HClO$_4$ was obtained by recording the ESI(+)-MS of an acetone solution (with 1% MeCN and 0.3 equiv of HClO$_4$/BrBzOH) of the Pd^{II} complex **2**·OBzBr (**A**$_{Br}$, Scheme 1), which neither intercepts [**2**·OBzBr+H$^+$] nor its Pd^{IV} isomer, homologue of **1**, [Pd(*O,N,C*-L)(*C,O*-C$_6$H$_4$CO$_2$-2)Br] (**1**$_{Br}$). This means that (1) **2**·OBzBr, which we have isolated and characterized by X-diffraction,[29] reacts with HClO$_4$ replacing HOBzBr, such as we anticipated for its homologue **2**·OBzI and (2) that it does not convert into **1**$_{Br}$, at difference of **2**·OBzI (Scheme 1); we had concluded the same when we studied its ^{1}H NMR spectrum. In summary, *the aryl-Pd^{IV} complex [1+H$^+$] is formed in the stoichiometric reaction 2·OClO$_3$ + IBzOH, in the presence of HClO$_4$, since the peaks around 562 m/z are mainly, if not exclusively, corresponding to such Pd^{IV} ion.* As the ^{1}H NMR of this reaction mixture does not detect **1**, the equilibrium **2**·OClO$_3$ + IBzOH ⇆ HClO$_4$ + **1** must be very displaced to the left. However, minute amounts of **1** in this equilibrium (shown by ESI-MS) would be enough to allow its role in the catalytic reaction (Scheme 2).

We have also monitored by ESI(+)-MS (acetone with 1% MeCN) the reaction using precatalyst **2**·OClO$_3$ after 20 min. Apart from peaks attributed to Ag$^+$ adducts and aggregate products, the peaks around 342, 355 and 562 m/z, found in the mixture **2**·OClO$_3$ + IBzOH, were also intercepted (see SI). In agreement with the above discussion, the peaks around 562 m/z *represent the first detection of an aryl-Pd^{IV} species in a catalytic process.*

We have also monitored by ESI(+)-MS (acetone with 1% MeCN) the catalytic reaction

using precatalyst [2'·NCMe]ClO$_4$ and detected Pd^{II} adducts [2'·N$_2$]$^+$, [2'·NCMe]$^+$,

[2'·N$_2$·MeOH]$^+$, [2'·NCMe·MeOH]$^+$ as well as a molecular ion of around 515 m/z that, as

in the case of the precatalyst 2·OClO$_3$, indicates the presence of the Pd^{IV} intermediate

[1'+H$^+$] (mean error of the 5 more intense peaks 1.8 ppm; see SI). Howewer, the relative

intensity of these peaks is much smaller than that corresponding to [1+H$^+$]. The minor

concentration of these intermediates could be related with the reaction rate; the faster it is,

the lower is the concentration of intermediates, other factors being similar. In fact, the

ESI(+)-MS of the stoichiometric reaction of 2'·NCMe with 10 equiv de IBzOH (acetone

with 1% MeCN and 0.3 equiv of HClO$_4$/IBzOH), detects the same group of peaks around

515 m/z but more intense than in the catalytic reaction. This means that the oxidative

addition is an equilibrium in which the Pd^{IV} complex exists in a ratio greater than that in the

catalytic reaction because it is not consumed by reacting with AgClO$_4$ and the olefin. This

also supports the involvement of Pd^{IV} in the catalytic cycle. All attempts to isolate 1' or its

acetato precursor by using the method we applied for its homologue 1 or 2·OAc were

unfruitful.

A tentative proposal for the mechanism. Although the present work did not intend to

study the mechanism of the reaction but providing support in favour of the existence of

some Pd^{IV} intermediate during this catalysis, we tentatively represent in Schemes 2 and 3

our proposal of mechanism. Complex 1 neither reacts appreciably with CH$_2$=CHCO$_2$Me

nor with AgClO$_4$ (by ^{1}H NMR). However, it does when the three reagents are present. We

think that the use of AgClO$_4$ is justified by the need to create a coordination vacancy

around Pd^{IV} to coordinate the olefin before the migratory insertion. Therefore, we postulate

that complex 1 reacts first with AgClO$_4$ to give a pentacoordinate complex, which reacts

with the olefin to afford the intermediate [A]ClO$_4$ (Scheme 2). The following steps

replicate those proposed in the Pd(0)/Pd^{II} cycle: migratory insertion of the aryl ligand to the

olefin and β-hydride elimination to give the Pd^{II} complex [**B**]ClO$_4$, which dissociates the ortho vinylated benzoic acid, regenerating the catalyst [**2**]ClO$_4$. The reaction from **1'** could follow a similar pathway (Scheme 3). DFT studies on Pd^{II}/Pd^{IV} catalytic cycles find that T-shaped complexes, like [**2**]ClO$_4$, are the active catalysts.[18] In agreement with our results, complex **1** is better described as an intermediate in the catalytic cycle rather than a precatalyst.

Conclusion

In conclusion, using the Pd^{IV} complex **1** or the Pd^{II} derivatives **2**·OAc, **2**·OClO$_3$, or [**2'**·NCMe]ClO$_4$ as precatalyst for the room temperature Heck-type synthesis of olefins (E)-ArCH=CHR from CH$_2$=CHR and 2-IC$_6$H$_4$CO$_2$H, we have succeeded in (1) the detection by ESI(+)-MS, for the first time, of some peaks mainly, if not exclusively, corresponding to aryl-Pd^{IV} species [**1**+H$^+$] during the catalytic reaction; to assume they were exclusively attributable to its Pd^{II} isomer [**2**·OBzI+H$^+$] is not tenable, on the basis of elemental chemical concepts and the negative test with **A**$_{Br}$, (2) the detection by ESI(+)-MS of peaks corresponding to the aryl-Pd(IV) complex **1'**; the fact that these peaks were weaker in the catalytic mixture than in the stoichiometric reaction [**2'**·NCMe]ClO$_4$ + 10 IBzOH also suggests the involvement of **1'** as intermediate in the catalytic cycle, (3) obtaining experimental data that exclude the intervention of soluble or insoluble nanoparticles of Pd or soluble Pd(0) complexes or Ag$^+$ as catalysts, (4) the detection of intermediates ([**2**·S]ClO$_4$ and [**2'**·S]ClO$_4$) in solution, the synthesis of their precursors ([**2**·OClO$_3$]ClO$_4$ and **2'**·NCMe]ClO$_4$, respectively) and their use as precatalysts, (5) studying the conversion (%) *vs* time for the catalytic synthesis of **3a** using three different precatalysts; the data establish the homogeneous nature of the catalysis and the following order of reaction rates depending on the precatalyst: [**2'**·NCMe]ClO$_4$ > **2**·OAc > **1**, and (6) changing the catalysis to heterogeneous by replacing the anion ClO$_4^-$ by TfO$^-$ or by increasing the temperature reaction in the absence of AgClO$_4$; these reactions differ from those using the

homogeneous precatalysts in the conversion *versus* time plots, their quenching in the presence of Hg and in the fact that we detect the corresponding HL^+ or HL'^+ salt. We are convinced that our catalytic reaction can not be taken as a model for most Heck-type catalytic reactions. Still, its value stands on the long awaited detection of an aryl-Pd^{IV} complex in a catalytic reaction, which is facilitated by the use of a Pd^{II} pincer complex and the use of IBzOH as the aryl halide. We expect our work will encourage those who have argued that some C–C coupling reactions could occur through a Pd^{II}/Pd^{IV} cycle, to find more examples like ours in order to establish the limits of this alternative to the main Pd^0/Pd^{II} mechanism.

Experimental Section

Complexes **1**, **2**·OAc,[29] and **2**·Cl[32] were obtained following previously described procedures. Compounds **3b** and **3c** were prepared as **3a**.[29] Their spectroscopic properties are in agreement with the data previously reported.[31] Details on the kinetic studies, poisoning experiments, NMR and ESI(+)-MS spectra are included in the SI. Chart 1 shows the atom numbering used in NMR assignments.

Unless otherwise stated, the reactions were carried out without precautions against light or atmospheric oxygen or moisture. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. NMR spectra were recorded on Brucker Avance 200, 300 or 400 spectrometers at room temperature. Chemical shifts were referred to TMS. NMR assignments were performed with the help of APT, HMQC and HMBC techniques. Complexes **1**,[29] **2**·OAc,[29] and **2**·Cl[32] were prepared following previously described procedures. Compounds **3b** and **3c** were prepared as for **3a**.[29] Their spectroscopical properties are in agreement with the data previously reported.[31]

Synthesis of [Pd(*O,N,C*-L)(OClO₃)]·1/4 CH₂Cl₂ (2·OClO₃). To a solution of 2·Cl (29.1 mg, 0.08 mmol) in CH_2Cl_2 (5 mL) was added $AgClO_4$ (34.4 mg, 0.17 mmol). The reaction mixture was vigorously stirred for 15 min and then filtered through Celite. The resulting solution was concentrated (1 mL) and the addition of Et_2O (6 mL) gave a suspension, which was filtered under N_2. The solid was washed with Et_2O and dried under a N_2 stream to give 3·OClO₃ as a yellow solid. Yield: 31.2 mg, 87%. Mp: 138 ºC dec. Λ_M = 81 ∧·cm²·mol⁻¹. IR (Nujol, cm⁻¹): $\widetilde{\nu}$(C=O) 1700, $\widetilde{\nu}$(C=N) 1604, $\widetilde{\nu}$(Cl–O) 1005. ¹H NMR (200 MHz, [D₆]acetone): ^{TM}8.48 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 7.99 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ =1.2 Hz), 7.89 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ =1.2 Hz), 3.50 (s, 2H, CH₂), 3.48 (s, 6H, OMe), 1.90 (s, 3H, Me). ¹H NMR (300 MHz, CDCl₃): ^{TM}8.19 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 7.80 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ =1.2 Hz), 7.65 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ =1.2 Hz), 3.75 (s, 2H, CH₂), 3.46 (s, 6H, OMe), 1.81 (s, 3H, Me). Anal. Calcd for $C_{11}H_{14}NO_7ClPd$·1/4CH₂Cl₂: C, 31.04; H, 3.36; N, 3.22. Found: C, 31.04; H, 3.27; N, 3.43.

Synthesis of [Pd(*O,N,C*-L')(NCMe)]ClO₄ ([2'·NCMe]ClO₄). To a mixture of IBzOH (168.7 mg, 0.68 mmol), $AgClO_4$ (141.0 mg, 0.68 mmol) and 1 (39.3 mg, 0.07 mmol) was added a solution of CH_2=CHCO₂Me (122.5 µL, 1.36 mmol) in acetone (10 mL). The mixture was stirred for 4 h in the dark and then filtered through Celite. The filtrate was concentrated (1 mL) and MeCN (1 mL) and Et_2O (20 mL) were added. The resulting precipitate was filtered off, washed with Et_2O (2x5 mL) and dried under N_2, giving orange [2'·NCMe]ClO₄. Yield: 21.2 mg, 76%. Mp: 148 ºC dec. IR (Nujol, cm⁻¹): $\widetilde{\nu}$(C≡N) 2328, $\widetilde{\nu}$(C=O) 1707, 1637, $\widetilde{\nu}$(C=N) 1594, $\widetilde{\nu}$(Cl–O) 1099. ¹H NMR (400 MHz, [D₆]acetone): ^{TM} 8.84 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz),   8.70 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 8.18 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 3.68 (s, 2 H, CH₂), 3.08 (s, 3 H, Me). ¹H NMR (200 MHz, [D₃]acetonitrile): ^{TM}8.40 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz),   8.14 (dd, 1 H, H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 8.03 (dd, 1 H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 3.61 (s, 2H,

CH$_2$), 2.85 (s, 3H, Me). ^{13}C{^{1}H} NMR (50.30 MHz, [D$_3$]acetonitrile): ^{TM}200.0 (s, C6), 197.7 (s, C2), 156.9 (s, C1), 156.1 (s, C7), 143.9 (s, C4), 129.8 (s, C3), 126.5 (s, C5), 39.0 (s, CH$_2$), 28.5 (s, Me). Anal. Calcd for C$_{11}$H$_{11}$N$_2$O$_6$ClPd: C, 32.30; H, 2.71; N, 6.85. Found: C, 32.33; H, 2.80; N, 6.82.

Acknowledgements

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