

Formation of anionic palladium(0) complexes ligated by the trifluoroacetate ion and their reactivity in oxidative addition

Christian Amatore ^{a,*}, Anny Jutand ^{*,a}, Frédéric Lemaître ^a, Jean Luc Ricard ^a,
Sebastian Kozuch ^b, Sason Shaik ^b

^a *Département de Chimie, Ecole Normale Supérieure, UMR CNRS 8640, 24 Rue Lhomond, F-75231 Paris Cedex 5, France*

^b *Department of Organic Chemistry, Lise Meitner-Minerva Center for Computational Quantum Chemistry, Hebrew University, Jerusalem, Israel*

Received 30 March 2004; accepted 8 May 2004

Available online 2 July 2004

Abstract

As established previously for $\text{Pd}(\text{OAc})_2$, Pd^0 complexes are formed in situ from $\text{Pd}(\text{OCOCF}_3)_2$ and n equiv. triarylphosphines ($4\text{-Z-C}_6\text{H}_4\text{)}_3\text{P}$ ($\text{Z}=\text{CF}_3, \text{F}, \text{Cl}, \text{H}, \text{CH}_3; n \geq 3$). The phosphines are the intramolecular reducing agents and are oxidized to triarylphosphine oxides. The generated Pd^0 complexes are anionic species ligated by the trifluoroacetate anion: $\text{Pd}^0(\text{PAR}_3)_n(\text{OCOCF}_3)^- (n=2 \text{ or } 3)$. $\text{Pd}^0(\text{PAR}_3)_2(\text{OCOCF}_3)^-$ is the reactive species involved in the oxidative addition to PhI . This leads to *trans*- $\text{PhPd}(\text{OCOCF}_3)(\text{PPh}_3)_2$, involved in equilibrium with the cationic complex *trans*- $[\text{PhPd}(\text{PPh}_3)_2(\text{DMF})]^+$, instead of the expected *trans*- $\text{PhPdI}(\text{PPh}_3)_2$ complex. The existence of anionic Pd^0 complexes ligated by the acetate or trifluoroacetate ions delivered by the precursors $\text{Pd}(\text{OAc})_2$ or $\text{Pd}(\text{OCOCF}_3)_2$, respectively, as well as their comparative reactivity in oxidative additions are consistent with theoretical DFT calculations.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Palladium; Acetate; Trifluoroacetate; Oxidative addition; Mechanism; Kinetics

1. Introduction

In previous works, some of us provided experimental evidence of the formation of anionic Pd^0 complexes $\text{Pd}^0\text{L}_2(\text{OAc})^-$ ($\text{L}=\text{PPh}_3$ [1] or $\text{L}_2=\text{dppp}$ [2]) (instead of the postulated Pd^0L_2) from the catalytic precursor $\text{Pd}^{\text{II}}(\text{OAc})_2$ often used to catalyze Heck reactions (Schemes 1 and 2) [3].

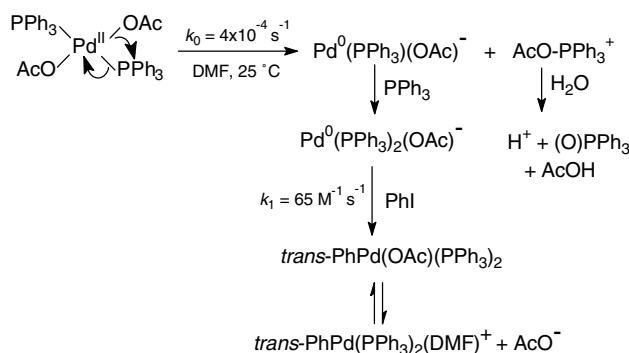
The existence and stability of the anionic complexes $\text{Pd}^0\text{L}_2(\text{OAc})^-$ ($\text{L}=\text{PPh}_3$ or $\text{L}_2=\text{dppp}$) has been confirmed recently on the basis of theoretical calculations (DFT) [4]. As a consequence of the formation of such anionic Pd^0 complexes ligated by the acetate ion, neutral complexes $\text{ArPd}(\text{OAc})(\text{PPh}_3)_2$ are generated during their

oxidative addition to aryl halides, ArX (Scheme 1) complexes [1c,1d], instead of the postulated ArPdXL_2 complexes [3]. In the bidentate series, the main complex formed in the oxidative addition is $\text{ArPd}(\text{dppp})((\text{O})\text{dppp})^+$ [2,3f] or $\text{ArPd}(\text{OAc})(\text{dppp})$ [2] when the oxidative addition is performed in the presence of a large excess of acetate ions which may be used as the base required in every Heck reactions (Scheme 2) [3].

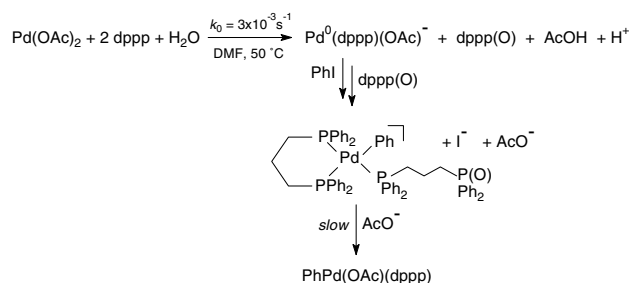
$\text{Pd}(\text{OCOCF}_3)_2$ associated with a few equivalent of phosphines is not very often used as catalytic precursor in Heck reactions, but in view of the above results, it was of interest to determine: (i) whether a Pd^0 complex was spontaneously generated from these mixtures and (ii) whether the less basic anion trifluoroacetate was able to coordinate the Pd^0 complex as AcO^- does, as well as (iii) the consequences on the reactivity of the anionic Pd^0 in oxidative addition. This was the purpose of the work that we report hereafter.

* Corresponding authors. Tel.: +33-1-4432-3872; fax: +33-1-4432-3325.

E-mail addresses: christian.amatore@ens.fr (C. Amatore), Anny.Jutand@ens.fr (A. Jutand).



Scheme 1.



Scheme 2.

2. Results and discussion

2.1. Evidence of the formation of anionic Pd^0 complexes from $\text{Pd}(\text{OCOCF}_3)_2$ and n equiv. PPh_3 ($n=4$)

The complex $\text{Pd}^{\text{II}}(\text{OCOCF}_3)_2(\text{PPh}_3)_2$ was formed upon addition of 4 equiv. PPh_3 to $\text{Pd}(\text{OCOCF}_3)_2$ (2 mM) in DMF containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M). It was characterized by its reduction peak at $E_{\text{red}}^{\text{p}} = -1.14$ V vs SCE. This complex was not stable in DMF, as attested by the decrease of its reduction peak current (proportional to concentration) with time. The cyclic voltammograms showed also another reduction peak which appeared at -0.3 V vs SCE and whose reduction current increased with time. This current due to the reduction of protons (vide supra) was suppressed by the initial addition of a base NEt_3 (3 equiv.) to the mixture $\text{Pd}(\text{OCOCF}_3)_2$ and 4 equiv. PPh_3 . Under such conditions, the decrease of the reduction current of $\text{Pd}^{\text{II}}(\text{OCOCF}_3)_2(\text{PPh}_3)_2$ could be precisely observed. Concomitantly to this decrease, an oxidation peak O_1 appeared at $E_{\text{ox}}^{\text{p}} = +0.06$ V vs SCE whose oxidation peak current increased with time (Fig. 1(a)). This evidences that a Pd^0 complex was generated in situ from $\text{Pd}^{\text{II}}(\text{OCOCF}_3)_2(\text{PPh}_3)_2$ in DMF. The ensuing Pd^0 complex was stable when generated from the mixture $\text{Pd}(\text{OCOCF}_3)_2$ and 4 equiv. PPh_3 in DMF containing NEt_3 (3 equiv.). Its formation was rather fast, being complete within 30 min at 25 °C.

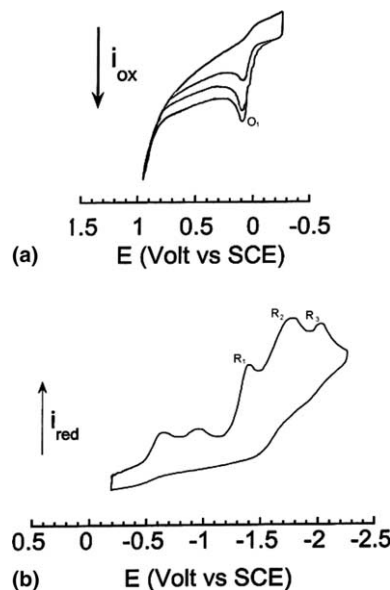
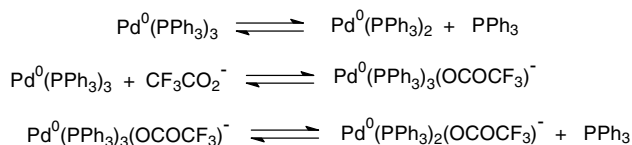


Fig. 1. Cyclic voltammetry performed in DMF (containing $n\text{Bu}_4\text{NBF}_4$, 0.3 M) at a steady gold disk electrode (0.5 mm diameter) with a scan rate of 0.5 V s^{-1} , at 25 °C: (a) oxidation peak of the Pd^0 complex generated from $\text{Pd}(\text{OCOCF}_3)_2$ (2 mM) and PPh_3 (8 mM) in the presence of NEt_3 (6 mM), from top to bottom: 3, 17, 32 min after mixing; (b) reduction of the species formed in the oxidative addition of PhI (2 mM) to the Pd^0 complex generated in situ from $\text{Pd}(\text{OCOCF}_3)_2$ (2 mM) and PPh_3 (8 mM) in the presence of NEt_3 (6 mM). R_1 , reduction of OCOCF_3^- ; R_2 , reduction of $[\text{PhPd}(\text{PPh}_3)_2(\text{DMF})]^+$; R_3 , reduction of $[\text{PhPd}(\text{OCOCF}_3)(\text{PPh}_3)_2]$.

The ^{31}P NMR spectrum of the resulting Pd^0 solution exhibited two signals (i) a broad singlet at $+21.48$ ppm ($\Delta\nu_{1/2} = 350$ Hz) which disappeared upon addition of phenyl iodide and was then assigned to Pd^0 complexes involved in an equilibrium with PPh_3 whose signal was not observed and (ii) a sharp singlet at $+25.44$ ppm characteristic of triphenylphosphine oxide. When the Pd^0 complexes were generated from $\text{Pd}(\text{OCOCF}_3)_2$ and 10 equiv. PPh_3 , the free PPh_3 (usually at -5.24 ppm) was still not detected which confirms that PPh_3 was involved in a dynamic equilibrium with Pd^0 complexes. Moreover, the broad signal of the Pd^0 complexes shifted to upper field at $+1.90$ ppm and became thinner ($\Delta\nu_{1/2} = 270$ Hz) in agreement with a higher contribution of PPh_3 in the dynamic equilibrium.

To better characterize the Pd^0 complex(es) generated from $\text{Pd}(\text{OCOCF}_3)_2$ and PPh_3 , $n\text{Bu}_4\text{NOCOCF}_3$ was added to a solution of $\text{Pd}^0(\text{PPh}_3)_4$ (20 mM) in DMF containing acetone- d_6 10% and the resulting Pd^0 complex(es) were characterized by ^{31}P NMR spectroscopy. The broad ^{31}P NMR signal ($\Delta\nu = 450$ Hz) of $\text{Pd}^0(\text{PPh}_3)_4$ in DMF observed at $+11$ ppm, characteristic of the equilibrium between $\text{Pd}^0(\text{PPh}_3)_3$, $\text{Pd}^0(\text{PPh}_3)_2$ and PPh_3 (Scheme 3) [5] was shifted to $+8.4$ ppm upon addition of $n\text{Bu}_4\text{NOCOCF}_3$ (1 equiv.). No free phosphine was detected. This signal was shifted to upper and upper field upon increasing the amount of added $n\text{Bu}_4\text{NOCOCF}_3$.



Scheme 3.

This establishes that the anion CF_3CO_2^- coordinates Pd^0 complexes to generate anionic species which remained in dynamic equilibrium with PPh_3 (Scheme 3).

On the other hand, after addition of 2 equiv. of $\text{CF}_3\text{CO}_2\text{Na}$ to $\text{Pd}^0(\text{PPh}_3)_4$ (10 mM) in DMF containing acetone- d_6 10%, two singlets were observed in the ^{19}F NMR spectrum, located at 102.935 and 102.920 ppm which differed from the signal of the free CF_3CO_2^- located at 102.985 (Fig. 2). After addition of 10 equiv. of $\text{CF}_3\text{CO}_2\text{Na}$ to $\text{Pd}^0(\text{PPh}_3)_4$, only one singlet was observed at 102.916 ppm (Fig. 2). This is a further evidence

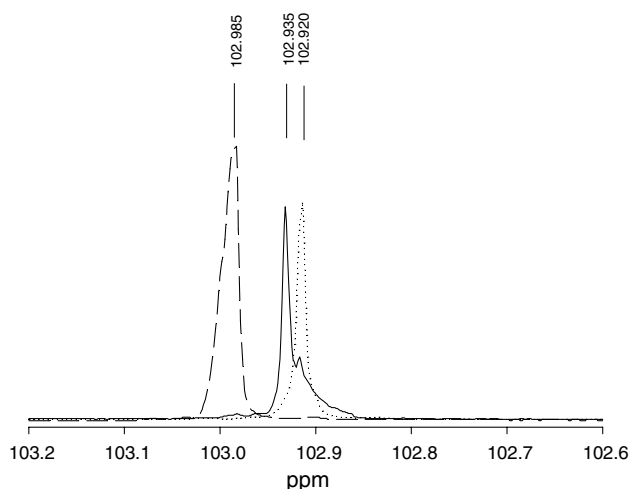


Fig. 2. ^{19}F NMR spectra (235.31 MHz, CFCl_3 as an external reference and $n\text{Bu}_4\text{NBF}_4$ as an internal reference) in DMF and acetone- d_6 10%: $\text{CF}_3\text{CO}_2\text{Na}$ (20 mM) alone (dashed line); $\text{Pd}^0(\text{PPh}_3)_4$ (10 mM) in the presence of 2 equiv. (solid line) and 10 equiv. (dotted line) of $\text{CF}_3\text{CO}_2\text{Na}$.

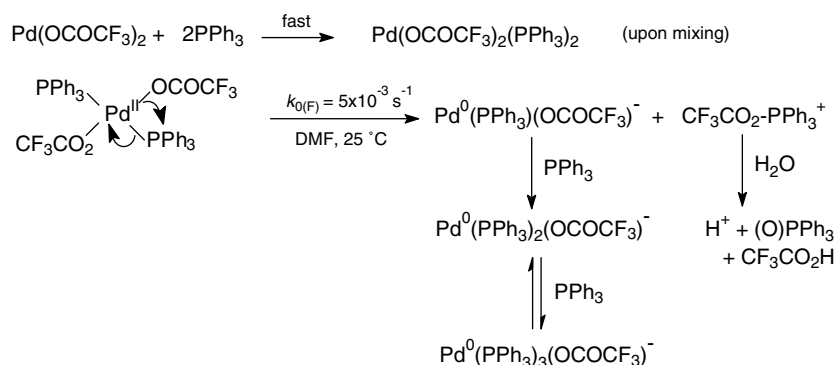
of the formation of the anionic species involved in the equilibrium of Scheme 3. The ^{19}F NMR spectrum of the Pd^0 complexes generated from $\text{Pd}(\text{OCOCF}_3)_2$ and four PPh_3 in DMF exhibited only one ^{19}F NMR singlet at 102.92 ppm, similar to that observed above.

In the light of these experiments, the Pd^0 complexes generated in situ by addition of excess PPh_3 to $\text{Pd}(\text{OCOCF}_3)_2$ may be characterized as anionic species ligated by the trifluoroacetate ion. They are involved in equilibrium which was fast compared to the time scale of the cyclic voltammetry because a single oxidation peak O_1 was observed (Fig. 1(a)).

The stability of the two anionic species $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$ and $\text{Pd}^0(\text{PPh}_3)_3(\text{OCOCF}_3)^-$ has been confirmed through DFT calculations (Pd–O bond length: 2.37 and 2.40 Å in $\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})$ and $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$, respectively; dissociation energy: 10.5 and 4.8 kcal mol $^{-1}$ for $\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})^-$ and $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$, respectively) [4].

2.2. Rate and mechanism of the formation of the anionic Pd^0 complexes from $\text{Pd}(\text{OCOCF}_3)_2$ and n equiv. (4- Z - C_6H_4) $_3\text{P}$ ($n \geq 3$)

The apparent first-order rate constant $k_{0(\text{F})}$ of the formation of the anionic Pd^0 complex was determined by amperometry at a rotating gold disk electrode polarized at +0.2 V vs SCE, i.e., on the plateau of the oxidation wave of the Pd^0 complexes, as done for $\text{Pd}(\text{OAc})_2$ [1a,1b,1d]. The rate constant did not vary significantly with the PPh_3 concentration, thus indicating a reaction order zero for PPh_3 and with the $\text{Pd}(\text{OCOCF}_3)_2$ concentration, in agreement of a reaction order one for Pd^{II} . This demonstrates that $k_{0(\text{F})}$ was a true first-order rate constant featuring the intramolecular reduction of the Pd^{II} to Pd^0 by the phosphine, occurring in the complex $\text{Pd}(\text{OCOCF}_3)_2(\text{PPh}_3)_2$ (Scheme 4) as previously established for $\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2$ (Scheme 1) [1a,1b,1d]. The hydrolysis of the phosphonium salt produced some trifluoroacetic acid whose proton reduction was detected by cyclic voltammetry in the absence of NEt_3 (vide supra).



Scheme 4. Mechanism of the formation of anionic Pd^0 complexes from $\text{Pd}(\text{OCOCF}_3)_2$ and four PPh_3 .

The value of $k_{0(F)} = 5(\pm 1) \times 10^{-3} \text{ s}^{-1}$ (DMF, 25 °C) indicates that the formation of the Pd^0 from $\text{Pd}(\text{OCOCF}_3)_2$ was ca. 10 times faster than that obtained from $\text{Pd}(\text{OAc})_2$ ($k_0 = 4 \times 10^{-4} \text{ s}^{-1}$ in DMF, 25 °C [1b]). This suggests an easier cleavage of the Pd–O bond during the intramolecular reductive elimination step, in agreement with the electron withdrawing property of CF_3 .

Pd^0 complexes were also generated in situ in DMF containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M) from $\text{Pd}(\text{OCOCF}_3)_2$ associated with various triarylphosphine ligands ($4\text{-Z-C}_6\text{H}_4)_3\text{P}$ whose aryl group had a substituent Z in the *para* position. They were detected and characterized by their oxidation peak at a steady gold disk electrode at the scan rate of 0.5 V s^{-1} ($\text{Z}=\text{Me}$: $E_{\text{ox}}^{\text{p}} = +0.01 \text{ V}$; $\text{Z}=\text{H}$: $E_{\text{ox}}^{\text{p}} = +0.12 \text{ V}$; $\text{Z}=\text{Cl}$: $E_{\text{ox}}^{\text{p}} = +0.30 \text{ V}$; $\text{Z}=\text{CF}_3$: $E_{\text{ox}}^{\text{p}} = +0.64 \text{ V}$ vs SCE). As expected, the Pd^0 complexes were more easily oxidized when the phosphine was more electron rich. The rate constant $k_{0(F)}^{\text{Z}}$ of the formation of the Pd^0 complexes was determined as described above. Whereas a linear Hammett plot was obtained previously for the formation of the Pd^0 complex from $\text{Pd}(\text{OAc})_2(\text{PAr}_3)_2$ ($\rho = +2.4$) thus establishing that the rate of formation of the Pd^0 complex was faster when the phosphine was less electron rich, the Hammett correlation was not linear in the case of $\text{Pd}(\text{OCOCF}_3)_2(\text{PAr}_3)_2$ (Fig. 3(a)). When Z was an electron withdrawing group, the slope was positive. The driving force of the reductive elimination should then be the attack of the trifluoroacetate ligand on $(4\text{-Z-C}_6\text{H}_4)_3\text{P}$ as established for $\text{Pd}(\text{OAc})_2(\text{PAr}_3)_2$. Conversely, the result with $\text{Z}=\text{Me}$ suggests that the slope is negative when Z is an electron donor group. This evidence that the driving force of the reductive elimination should be the attack of the electron rich $(4\text{-Z-C}_6\text{H}_4)_3\text{P}$ on the electron deficient trifluoroacetate ligand.

2.3. Rate and mechanism of the oxidative

addition of PhI to the anionic $\text{Pd}^0(\text{PAr}_3)_n(\text{OCOCF}_3)^-$ ($n = 2, 3$) complexes in DMF

The mechanism of the oxidative addition of PhI to the Pd^0 complexes generated from $\text{Pd}(\text{OCOCF}_3)_2$ and n equiv. PPh_3 was investigated in DMF and in the presence of a base (NEt_3) to neutralize the protons generated by the hydrolysis of the phosphonium salt (Scheme 4) which might interact with the anionic Pd^0 complexes as it has been observed for $\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})^-$ [1d]. The oxidative addition was monitored by amperometry at a rotating disk electrode polarized on the plateau of the oxidation wave of the anionic Pd^0 complexes ($C_0 = 2 \text{ mM}$) after addition of PhI (1 equiv.) as performed in the case of $\text{Pd}(\text{OAc})_2$ [1]. The ensuing plot of $1/x = [\text{Pd}^0]_0/[\text{Pd}^0]$ vs time was linear (Fig. 3(b)) in agreement with the expectation for a bimolecular reaction performed under stoichiometric conditions. k_{exp} was determined from the slope of the straight line: $1/x = k_{\text{exp}}t + 1$.

The oxidative addition was slower when the PPh_3 concentration was increased, establishing that $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$ was the reactive complex (Scheme 5) so that $k_{\text{exp}} = K_{1(F)}k_{1(F)}C_0/[\text{PPh}_3]$.

The value of the rate constant $k_{1(F)}$ was determined along the same procedure when the oxidative addition was performed under stoichiometric conditions with $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$ generated from $\text{Pd}(\text{OCOCF}_3)_2$ ($C_0 = 2 \text{ mM}$) and 3 equiv. PPh_3 . Indeed, due to the oxidation of one PPh_3 to $(\text{O})\text{PPh}_3$, the complex $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$ was then generated quantitatively in the absence of free PPh_3 ligand. One has then: $1/x = k_{1(F)}C_0t + 1$, from which it followed that:

$$k_{1(F)} = 81 \text{ M}^{-1} \text{ s}^{-1} \text{ (DMF, 25 °C)}.$$

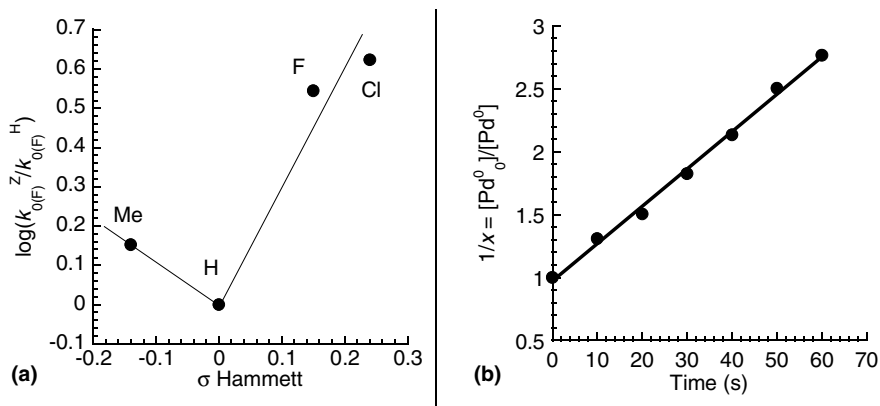
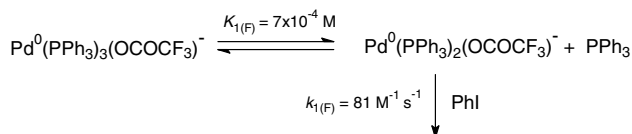


Fig. 3. (a) Hammett plot for the formation of the Pd^0 complex from $\text{Pd}(\text{OCOCF}_3)_2$ and 14 equiv. $(4\text{-Z-C}_6\text{H}_4)_3\text{P}$ in the presence of NEt_3 (3 equiv.) in DMF at 25 °C. The rate constant $k_{0(F)}^{\text{Z}}$ of the formation of the Pd^0 complex was determined by amperometry at a rotating gold disk electrode (2 mm diameter, $\omega = 105 \text{ rad s}^{-1}$) polarized on the oxidation wave of the Pd^0 complex. The increase of the oxidation current was recorded vs time. (b) Kinetics of the oxidative addition of PhI (1 equiv.) to the Pd^0 complexes generated from $\text{Pd}(\text{OCOCF}_3)_2$ ($C_0 = 2 \text{ mM}$) and 14 equiv. PPh_3 in the presence of NEt_3 (3 equiv.) in DMF at 25 °C. Plot of $1/x = [\text{Pd}^0]_0/[\text{Pd}^0]$ vs time ($[\text{Pd}^0]_0/[\text{Pd}^0] = i_0/i_t$ with i_0 : initial oxidation current of Pd^0 and i_t : oxidation current of Pd^0 at t). $1/x = k_{\text{exp}}t + 1$.



Scheme 5. Mechanism of the oxidative addition of PhI to the anionic Pd^0 complexes generated from $\text{Pd}(\text{OCOCF}_3)_2$ and $n\text{PPh}_3$ ($n \geq 4$) in DMF (25 °C).

The value of the equilibrium constant $K_{1(\text{F})}$ was determined from the kinetics of an oxidative addition performed under stoichiometric conditions with $\text{Pd}^0(\text{PPh}_3)_3(\text{OCOCF}_3)^-$ generated from $\text{Pd}(\text{OCOCF}_3)_2$ ($C_0 = 2 \text{ mM}$) and 14 equiv. PPh_3 . Then $1/x = k_{1(\text{F})}K_{1(\text{F})}C_0t/[\text{PPh}_3] + 1$ with $[\text{PPh}_3] = 11 \text{ mM}$. Using the above $k_{1(\text{F})}$ value, this afforded:

$$K_{1(\text{F})} = 7 \times 10^{-4} \text{ M (DMF, 25 °C)}.$$

The values of the rate constants $k_{1(\text{F})}$ and equilibrium constants $K_{1(\text{F})}$ are gathered in Table 1 and compared to those of k_1 and K_1 previously determined with $\text{Pd}(\text{OAc})_2$ as precursor [1d]. $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$ is intrinsically slightly more reactive than $\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})^-$ since $k_{1(\text{F})} > k_1$ (see columns 2 and 3, respectively, in Table 1). This result was not expected since the complex $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$ should be less electron rich than $\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})^-$. The slightly higher intrinsic reactivity of $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$ suggests that its Pd–O bond is weaker than that in $\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})^-$ so that its reactivity would be closer to that of the naked $\text{Pd}^0(\text{PPh}_3)_2$. This was confirmed by DFT calculations since the theoretical dissociation energy of $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$ was found to be less than that of $\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})^-$ (viz., 4.8 vs 10.5 kcal mol⁻¹, vide supra) [4].

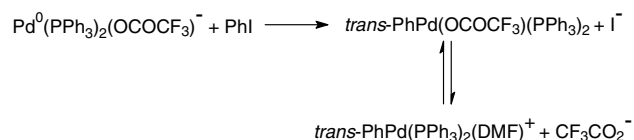
Interestingly, in the presence of excess PPh_3 ($n \geq 4$) the oxidative addition of PhI to the Pd^0 generated from $\text{Pd}(\text{OAc})_2$ was faster than to the Pd^0 obtained from $\text{Pd}(\text{OCOCF}_3)_2$. Indeed, the overall reactivity is then given by the value of k_1K_1 (Scheme 5) and $k_1K_1 > k_{1(\text{F})}K_{1(\text{F})}$ (see columns 2 and 3, respectively, in Table 1). On one hand, one has: $k_1 < k_{1(\text{F})}$, but on the other hand: $K_1 > K_{1(\text{F})}$. The overall higher reactivity of the Pd^0 complex generated from $\text{Pd}(\text{OAc})_2$ originates from a higher concentration of the reactive species

$\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})^-$ than that of $\text{Pd}^0(\text{PPh}_3)_2(\text{OCOCF}_3)^-$ in their respective equilibrium despite the slight higher intrinsic reactivity of the second species.

When $\text{Pd}(\text{OCOCF}_3)_2$ was considered, the $\text{Pd}^0[(4\text{-Z-C}_6\text{H}_4)_3\text{P}]_2(\text{OCOCF}_3)^-$ complexes were, as expected, more reactive when the phosphine was more electron rich ($\text{Z} = \text{Me} > \text{H} > \text{Cl}$) (see $k_{1(\text{F})}$ in columns 3–5 of Table 1). The same trend was observed in the presence of excess ligand (see $k_{1(\text{F})}K_{1(\text{F})}$ in columns 3–5 of Table 1), since $K_{1(\text{F})}$ decreased also in the same order.

2.4. Characterization of the phenyl-palladium(II) complexes generated in the oxidative addition of PhI to the anionic $\text{Pd}^0(\text{PAr}_3)_n(\text{OCOCF}_3)^-$ ($n = 2, 3$) complexes in DMF

The oxidative addition of PhI to the anionic $\text{Pd}^0(\text{PPh}_3)_3(\text{OCOCF}_3)^-$ generated from $\text{Pd}^0(\text{OCOCF}_3)_2$ (2 mM) and 4 equiv. PPh_3 in the presence of NEt_3 (3 equiv.) in DMF containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M) was monitored by cyclic voltammetry at a steady gold disk electrode at the scan rate of 0.5 V s⁻¹. At the end of the oxidative addition, the oxidation peak of the Pd^0 complex at +0.06 V was no longer observed but a new oxidation peak was observed at +0.50 V which could be readily assigned to the oxidation of iodide ions by comparison with the oxidation of an authentic sample of $n\text{Bu}_4\text{NI}$ performed under similar conditions. This suggests that iodide ions were released in the course of the oxidative addition (Scheme 6). In the reduction part of the voltammogram, three reduction peaks were observed (Fig. 1(b)). The first one at $E_{\text{R}_1}^p = -1.40 \text{ V}$ vs SCE characterizes the reduction of the anion CF_3CO_2^- by comparison to an authentic sample of $n\text{Bu}_4\text{NO-COCF}_3$. The second one at $E_{\text{R}_2}^p = -1.81 \text{ V}$ vs SCE characterizes the cationic complex $[\text{PhPd}(\text{PPh}_3)_2(\text{DMF})]^+$.



Scheme 6. Mechanism of the oxidative addition of PhI to the anionic Pd^0 complex ligated by the trifluoroacetate ion.

Table 1

Comparative reactivity of anionic Pd^0 complexes generated from palladium(II) carboxylates and triarylphosphines in their oxidative addition to PhI (DMF, 25 °C) (see Scheme 5 as an example)

Precursor Ligand	$\text{Pd}(\text{OAc})_2$ PPh_3	$\text{Pd}(\text{OCOCF}_3)_2$ PPh_3	$\text{Pd}(\text{OCOCF}_3)_2$ (4-Me-C ₆ H ₄) ₃ P	$\text{Pd}(\text{OCOCF}_3)_2$ (4-Cl-C ₆ H ₄) ₃ P
k_1 (M ⁻¹ s ⁻¹)	65 ± 2	81 ± 4	92 ± 2	21
K_1 (M)	1.9 × 10 ⁻³	0.7 × 10 ⁻³	2.7 × 10 ⁻³	0.9 × 10 ⁻³
k_1K_1 (s ⁻¹)	123	57	248	19

Such complex was already observed in its equilibrium with $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$ [1c,1d]. The third one at $E_{\text{R}_3}^{\text{p}} = -2.05$ V vs SCE characterized then the remaining fraction of the neutral complex $\text{PhPd}(\text{OCOCF}_3)(\text{PPh}_3)_2$ which is in equilibrium with the two previous species (Scheme 6). The ratio of the two reduction peak currents $i_{\text{R}_2}/i_{\text{R}_3}$ increased as the scan was decreased as in a CE mechanism [6], establishing the existence of the equilibrium in Scheme 6. At the same scan rate, the ratio $i_{\text{R}_2}/i_{\text{R}_3}$ was higher for $\text{PhPd}(\text{OCOCF}_3)(\text{PPh}_3)_2$ than for $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$ [1c,1d], suggesting that $\text{PhPd}(\text{OCOCF}_3)(\text{PPh}_3)_2$ dissociated more easily to the cationic complex $[\text{PhPd}(\text{PPh}_3)_2(\text{DMF})]^+$ than $\text{PhPd}(\text{OAc})(\text{PPh}_3)_2$. In other words, as expected, the affinity of the trifluoroacetate ion for the Pd^{II} center is less than that of the acetate ion. The complex $\text{PhPd}(\text{OCOCF}_3)(\text{PPh}_3)_2$ was also characterized by a ^{31}P NMR singlet at +22.56 ppm in DMF and acetone- d_6 (10%), attesting a *trans* structure for the two magnetically equivalent phosphines. The complex *trans*- $\text{PhPdI}(\text{PPh}_3)_2$ (23.37 ppm) could not be observed except upon addition of an excess of iodide ions.

Therefore, the oxidative addition of PhI to the anionic Pd^0 complex ligated by the trifluoroacetate ion did not afford the usual *trans*- $\text{PhPdI}(\text{PPh}_3)_2$ complex [3] but *trans*- $\text{PhPd}(\text{OCOCF}_3)(\text{PPh}_3)_2$ together with the cationic complex *trans*- $[\text{PhPd}(\text{PPh}_3)_2(\text{DMF})]^+$ (Scheme 6), emphasizing the important role played by the anion CF_3CO_2^- delivered by the Pd^{II} precursor $\text{Pd}(\text{OCOCF}_3)_2$ as already observed for $\text{Pd}(\text{OAc})_2$ [1].

3. Conclusion

Anionic $\text{Pd}^0(\text{PAR}_3)_n(\text{OCOCF}_3)^- (n=2, 3)$ complexes were generated whatever the phosphine associated to the Pd^{II} precursor $\text{Pd}(\text{OCOCF}_3)_2$ by an intramolecular reduction by the phosphine in $\text{Pd}(\text{OCOCF}_3)_2(\text{PAR}_3)_2$. The anionic complex $\text{Pd}^0(\text{PAR}_3)_2(\text{OCOCF}_3)^-$ is the reactive species in the oxidative addition to PhI . The electronic properties of the triarylphosphine ligands affect both the kinetics of formation of the anionic Pd^0 complex and its reactivity in oxidative addition. The oxidative addition to PhI does not afford the expected *trans*- $\text{PhPdI}(\text{PPh}_3)_2$ but *trans*- $\text{PhPd}(\text{OCOCF}_3)(\text{PPh}_3)_2$ which is in equilibrium with the cationic complex *trans*- $[\text{PhPd}(\text{PPh}_3)_2(\text{DMF})]^+$.

These results are very reminiscent to those established for ionic $\text{Pd}^0(\text{PAR}_3)_n(\text{OAc})^- (n=2, 3)$ complexes generated from $\text{Pd}(\text{OAc})_2$. The rate of formation of $\text{Pd}^0(\text{PAR}_3)_2(\text{OCOCF}_3)^-$ from $\text{Pd}(\text{OCOCF}_3)_2$ is higher than the rate of formation of $\text{Pd}^0(\text{PAR}_3)_2(\text{OAc})^-$ from $\text{Pd}(\text{OAc})_2$. $\text{Pd}^0(\text{PAR}_3)_2(\text{OCOCF}_3)^-$ is intrinsically slightly more reactive than $\text{Pd}^0(\text{PAR}_3)_2(\text{OAc})^-$ in oxidative addition with PhI . This shows that: (i) the rate of formation of the anionic Pd^0 complexes, (ii) the rate of their oxidative

addition with PhI and (iii) the equilibrium constant between *trans*- $\text{PhPd}(\text{OCOZ})(\text{PPh}_3)_2$ ($\text{Z} = \text{CH}_3$ or CF_3) and the cationic complex *trans*- $[\text{PhPd}(\text{PPh}_3)_2(\text{DMF})]^+$ generated in the oxidative addition are affected by the carboxylate anion introduced by the Pd^{II} precursor whose nature plays then a crucial role.

4. Experimental

4.1. General

^{31}P NMR spectra were recorded on a Bruker spectrometer (101 MHz) in DMF containing 10% of acetone- d_6 . ^{19}F NMR were recorded on a Bruker spectrometer (235.31 MHz) using CFCl_3 as an external reference and $n\text{Bu}_4\text{NBF}_4$ as an internal reference in DMF containing 10% of acetone- d_6 . Cyclic voltammetry was performed with a home made potentiostat and a wave form generator Tacussel GSTP4. The cyclic voltammograms were recorded on a Nicolet 301 oscilloscope.

4.2. Chemicals

DMF was distilled from calcium hydride under vacuum and kept under argon. $\text{Pd}(\text{OCOCF}_3)_2$, the phosphine (4- $\text{Z}-\text{C}_6\text{H}_4$) $_3\text{P}$ ($\text{Z} = \text{CF}_3$, F, Cl, H, CH_3), PhI , $n\text{Bu}_4\text{NI}$, $n\text{Bu}_4\text{NOCOCF}_3$, NaOCOCF_3 were commercial.

4.3. Electrochemical set-up and electrochemical procedure for voltammetry

Typical experiments were carried out in a three-electrode thermostated 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 filled with 3 ml of DMF containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M). 15 ml of degassed DMF containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M) were introduced into the cell followed by 10 mg (0.03 mmol) of $\text{Pd}(\text{OCOCF}_3)_2$, 37 mg (0.14 mmol) PPh_3 and 9 mg (0.09 mmol) NEt_3 . Cyclic voltammetry was performed at a steady gold disk electrode (0.5 mm diameter) at a scan rate of 0.5 Vs^{-1} , unless stated differently. Kinetic measurements for the Pd^0 formation were performed at a rotating gold disk electrode (2 mm diameter, $\omega = 105 \text{ rad s}^{-1}$) polarized at +0.2 V vs SCE by recording the increase of the oxidation current of the Pd^0 with time. Kinetic measurements for the reactivity of the Pd^0 with PhI in the oxidative addition were then performed under the same conditions by recording the decrease of the oxidation current of the Pd^0 , previously observed, with time after addition of 6 mg (0.03 mmol) PhI .

Acknowledgement

This work has been supported in part by the Centre National de la Recherche Scientifique (UMR CNRS-

ENS-UPMC 8640) and the Ministère de la Recherche (Ecole Normale Supérieure). The AFIRST (Association Franco-Israélienne pour la Recherche Scientifique et la Technologie) is thanked for a grant and for supporting F.L. post-doctoral grant (991 MAE CCF5).

References

- [1] (a) C. Amatore, A. Jutand, M.A. M'Barki, *Organometallics* 11 (1992) 3009;
(b) C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, *Organometallics* 14 (1995) 1818;
(c) C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, G. Meyer, *Organometallics* 14 (1995) 5605;
(d) C. Amatore, A. Jutand, *Acc. Chem. Res.* 33 (2000) 314.
- [2] C. Amatore, A. Jutand, A. Thuilliez, *Organometallics* 20 (2001) 3241.
- [3] (a) T. Hayashi, A. Kubo, F. Ozawa, *Pure Appl. Chem.* 64 (1992) 421;
(b) A. de Mejeire, F.E. Meyer, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 2379;
(c) W. Cabri, I. Candini, *Acc. Chem. Res.* 28 (1995) 2;
(d) G.T. Crisp, *Chem. Soc. Rev.* 27 (1998) 427;
(e) I.P. Beletskata, A.V. Cheprakov, *Chem. Rev.* 100 (2000) 3009;
(f) M. Larhed, A. Hallberg, in: E. Negishi (Ed.), *Handbook of Organopalladium Chemistry for Organic Synthesis*, vol. I, Wiley, New York, 2002, pp. 1133–1178 (Chapter IV.2).
- [4] S. Kozuch, S. Shaik, A. Jutand, C. Amatore, *Chem. Eur. J.*, 2004 (in press).
- [5] C. Amatore, A. Jutand, F. Khalil, M.A. M'Barki, L. Mottier, *Organometallics* 12 (1993) 3168.
- [6] (a) A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980 p. 136;
(b) C. Amatore, E. Carré, A. Jutand, *Acta Chem. Scand.* 52 (1998) 106.