Pure Appl. Chem., Vol. 82, No. 7, pp. 1393–1402, 2010.
doi:10.1351/PAC-CON-09-09-22

Mechanism of the oxidative addition of aryl halides to bis-carbene palladium(0) complexes*

Anny Jutand[1,‡], Julien Pytkowicz[2], Sylvain Roland[2], and
Pierre Mangeney[2]

[1]Department of Chemistry, Ecole Normale Supérieure, UMR CNRS-ENS-UPMC 8640, 24 Rue Lhomond, F-75231, Paris Cedex 5, France; [2]Paris Institute of Molecular Chemistry, UMR CNRS-UPMC 7201, Université Pierre et Marie Curie, Bât F, Pièce 665, BC 43, 4 Place Jussieu, F-75252, Paris Cedex 05, France

Abstract: Bis-*N*-heterocyclic carbenes Pd^0 complexes, $Pd^0(NHC)_2$, are efficient catalysts in Heck reactions performed with aryl bromides or chlorides. The $Pd^0(NHC)_2$ that are not stable are generated in situ from Pd^{II} precursors $PdY_2(NHC)_2$ (Y = halides) after a chemical reduction. The latter procedure can be mimicked by an electrochemical reduction. The transient $Pd^0(NHC_{Bn})_2$ is generated by electrochemical reduction of $PdY_2(NHC_{Bn})_2$, and its reactivity in oxidative addition to aryl bromides and chlorides is characterized by the same electrochemical technique with the determination of the rate constants. $Pd^0(NHC_{Bn})_2$ is found to be more reactive than the mixed complex $Pd^0(NHC_{Bn})(PPh_3)$. Both are the reactive species in an associative mechanism. Comparison with the isolated $Pd^0(NHC_{tBu})_2$ reveals that $Pd^0(NHC_{Bn})_2$ is more reactive than $Pd^0(NHC_{tBu})_2$ even if the latter reacts via the mono-carbene $Pd^0(NHC_{tBu})$ in a dissociative mechanism. This suggests that the formation of mono-carbene $Pd^0(NHC)$ is not a guarantee for a fast oxidative addition because it is always generated at low concentration in its equilibrium with the related nonreactive bis-carbene $Pd^0(NHC)_2$.

Keywords: kinetics; mechanism; *N*-heterocyclic carbene; palladium; oxidative addition.

INTRODUCTION

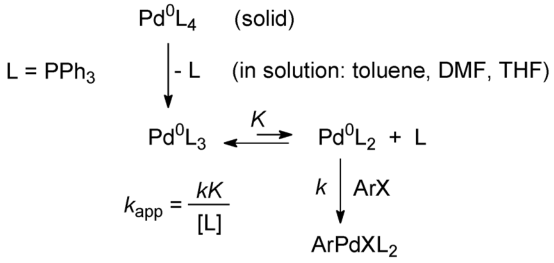
In the pioneer work by Fauvarque et al. [1], it was established from kinetic data that the reactive Pd^0 complex in oxidative additions to aryl halides (ArX) is a bis-ligated complex $Pd^0(PPh_3)_2$ generated in situ from the precursor $Pd^0(PPh_3)_4$. Even if $Pd^0(PPh_3)_2$ is very reactive, it is generated at low thermodynamic concentration from the major but unreactive species $Pd^0(PPh_3)_3$ [2] so that the overall oxidative addition performed from $Pd^0(PPh_3)_4$ is not characterized by the rate constant k but by an apparent rate constant $k_{app} = kK/[L]$ with a reaction order of –1 for the ligand [1,3] (Scheme 1). From the comparative reactivity of phenyl halides and triflate (Scheme 1), it emerges that PhCl cannot react with $Pd^0(PPh_3)_4$ in dimethylformamide (DMF) at 25 °C [4].

Consequently, if one needs to react aryl bromides or chlorides in palladium-catalyzed reactions, it is of interest to use ligands L which are more electron-donor than PPh_3 to enhance the reactivity of Pd^0L_2 and to start from isolated Pd^0L_2 complexes to bypass the equilibrium Pd^0L_2/Pd^0L_3, which is re-

---

*Paper based on a presentation at the 15th International Conference on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS-15), 26–31 July 2009, Glasgow, UK. Other presentations are published in this issue, pp. 1353–1568.

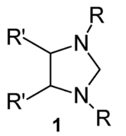
‡Corresponding author



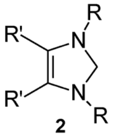
DMF, 25 °C	PhI	>>	PhOTf	>	PhBr	>>	PhCl
k_{app} ($M^{-1}s^{-1}$)	25		0.0017		0.001		no

Scheme 1 Rate and mechanism of the oxidative addition of $Pd(PPh_3)_4$ to phenyl halides and triflate.

sponsible for the low concentration and consequently low reactivity of Pd^0L_2. Isolated Pd^0L_2 species bearing bulky and electron-donor tertiary phosphines have been introduced by Hartwig [5]. It has been established that Pd^0L_2 (associative mechanism) [5,6] or Pd^0L (dissociative mechanism) [5] may react with aryl halides, depending on the ligand [5,6], the aryl halide [5], and the aryl halide concentration [7]. Later on, *N*-heterocyclic carbenes (NHCs) (**1**, **2**) were introduced by Herrmann et al. as ligands of palladium complexes [8]. Thanks to bulky electron-donor tertiary phosphines and NHC, it became possible to react aryl chlorides and bromides in most Pd-catalyzed reactions (Heck, Stille, cross-coupling, Sonogashira, Suzuki, etc.) [9]. A mini review on the mechanism of oxidative additions of aryl halides to $Pd^0(NHC)_2$ complexes is presented herein [10–12].



1

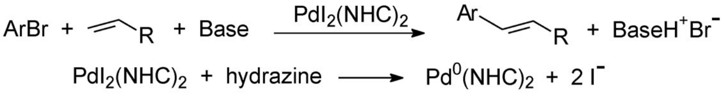


2

REACTIVITY OF BIS-CARBENE PALLADIUM(0) COMPLEXES

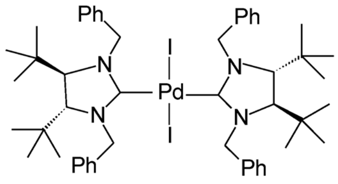
Generation of $Pd^0(NHC)_2$ complexes by chemical reduction of $PdY_2(NHC)_2$ precursors

NHC [13] (**1**, **2**) and related $Pd^0(NHC)_2$ [14] are mainly stable when the two nitrogen atoms bear bulky groups R. Herrmann et al. have used an unsaturated NHC (**2**) with R = Me and R' = H [8]. This ligand was introduced via a Pd^{II} precursor $PdI_2(NHC)_2$. In a Heck reaction performed from an aryl bromide, they observed that the slow reaction was dramatically accelerated upon addition of a chemical reductant such as hydrazine [8] (Scheme 2). This is a clear evidence for the formation of a Pd^0 complex as the reactive species in the oxidative addition to ArBr.



Scheme 2 Evidence for the formation of a Pd^0 complex ligated to NHC in Heck reactions.

A saturated NHC (named NHC_{Bn} in the following) has been introduced by Roland et al. [10] via $PdY_2(NHC_{Bn})_2$ (Y = I, Cl) precursors. They catalyze Heck reactions provided a chemical reductant such as formate is added to the reaction mixture.



$PdI_2(NHC_{Bn})_2$

From the X-ray structure of $PdI_2(NHC_{Bn})_2$, it is seen that the benzyl groups on the two N atoms are flexible and do not induce any steric hindrance around the Pd center [10]. This is probably why neither the ligand NHC_{Bn} nor $Pd^0(NHC_{Bn})_2$ can be isolated.

A problem arises: How can the reactivity of non-isolated $Pd^0(NHC_{Bn})_2$ in oxidative addition to aryl halides be investigated? The problem was solved by means of electrochemical techniques [10,12]. The electrochemical reduction of Pd^{II} precursors can indeed mimic the chemical reduction, which takes place in situ in catalytic reactions [15].

Generation of $Pd^0(NHC)_2$ complexes by electrochemical reduction of $PdY_2(NHC)_2$

The electrochemical reduction of $PdI_2(NHC_{Bn})_2$ (3 mM) in DMF at a steady gold disk electrode is displayed in Fig. 1. The cyclic voltammogram exhibits a single irreversible reduction peak R_1 [10].

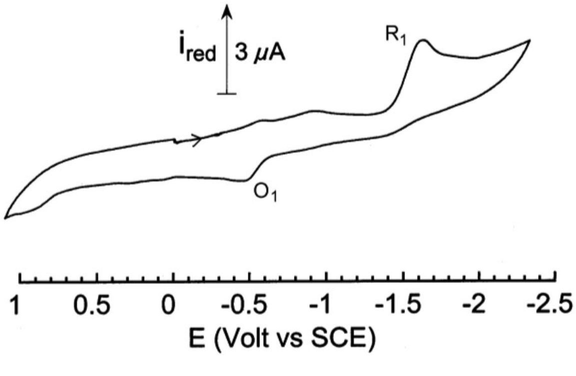
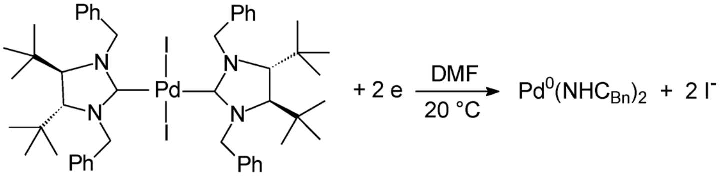


Fig. 1 Reduction of $PdI_2(NHC_{Bn})_2$ (3 mM) in DMF (containing $n$$Bu_4NBF_4$, 0.3 M) at a steady gold disk electrode (d = 0.5 mm) with a scan rate $v = 0.5$ V s^{-1}, at 20 °C.

Determination of the absolute number of electron(s), n, involved at R_1 gives $n = 1.8 \pm 0.1$ [16]. Consequently, the bielectronic reduction of $PdI_2(NHC_{Bn})_2$ affords a Pd^0 complex whose oxidation peak is observed on the reverse scan at O_1 (Fig. 1). Double-step chronoamperometry [15] reveals that the reduction of $PdI_2(NHC_{Bn})_2$ to $Pd^0(NHC_{Bn})_2$ is quantitative at the time scale of the electrochemical experiment. This shows that $Pd^0(NHC_{Bn})_2$ can be generated as a transient species [10] (Scheme 3).



Scheme 3 Electrochemical reduction of $PdI_2(NHC_{Bn})_2$.

Table 1 displays the oxidation peak potentials of Pd^0 complexes generated by the electrochemical reduction of $PdY_2(NHC_{Bn})_2$ (Y = I, Cl) or the mixed complex $PdI_2(NHC_{Bn})(PPh_3)$ [10]. When compared to other Pd^0 complexes ligated by PPh_3 [17], it is clearly seen that substitution of one or two NHC_{Bn} by PPh_3 gives Pd^0 complexes which are less and less easily oxidized. Even if oxidation peak potentials (not standard potentials) are compared, it is observed that the ligand NHC_{Bn} is more electron-donor than PPh_3, making the corresponding Pd^0 more electron-rich and consequently more easily oxidized. A higher reactivity of the Pd^0 ligated by NHC_{Bn} is thus expected in oxidative addition to aryl halides.

Table 1 Oxidation peak potentials of Pd^0 complexes in DMF at 20 °C.

Precursor	Pd^0	E^p_{Ox}, V vs. SCE[a]
$PdI_2(NHC_{Bn})_2$	$Pd^0(NHC_{Bn})_2$	–0.49
$PdCl_2(NHC_{Bn})_2$	$Pd^0(NHC_{Bn})_2$	–0.48
$PdI_2(NHC_{Bn})(PPh_3)$	$Pd^0(NHC_{Bn})(PPh_3)$	–0.15
$PdCl_2(PPh_3)_2$	$Pd^0(PPh_3)_2Cl^-$	+0.03
$Pd^0(dba)_2 + 2PPh_3$	$Pd^0(PPh_3)_2$	+0.14

[a]Determined at a steady gold disk electrode (*d* = 0.5 mm) with a scan rate of 0.5 V s^{-1}.

Reactivity of electrogenerated $Pd^0(NHC)_2$ in oxidative additions to aryl halides

When the electrochemical reduction of $PdI_2(NHC_{Bn})_2$ (3 mM) is performed in DMF in the presence of PhBr (3 mM), the oxidation peak O_1 of $Pd^0(NHC_{Bn})_2$ is no longer detected on the reverse scan (Fig. 2a) due to the oxidative addition [10] (Scheme 4). This reaction is pretty fast since it takes place within less than 5 s which is the time elapsed between the formation of $Pd^0(NHC_{Bn})_2$ at R_1 and its oxidation at O_1. When the scan rate *v* is increased, i.e., when the time scale allotted for the oxidative addition is decreased, the electrogenerated $Pd^0(NHC_{Bn})_2$ has less time to react in the oxidative addition before it is oxidized and some $Pd^0(NHC_{Bn})_2$ is recovered, as attested by the presence of its oxidation peak at O_1 (Fig. 2b). The time has been decreased from 5 to 0.25 s by increasing the scan rate from 0.5 V s^{-1} to 10 V s^{-1}, respectively (compare Figs. 2a and 2b).

$$\begin{tikzcd} PdI_2(NHC_{Bn})_2 + 2e \arrow[r, "DMF"] & Pd^0(NHC_{Bn})_2 + 2\,I^- \arrow[d, "ArX", "k"'] \\ & ArPdX(NHC_{Bn})_2 \end{tikzcd}$$

Scheme 4 Oxidative addition of the electrogenerated $Pd^0(NHC_{Bn})_2$.

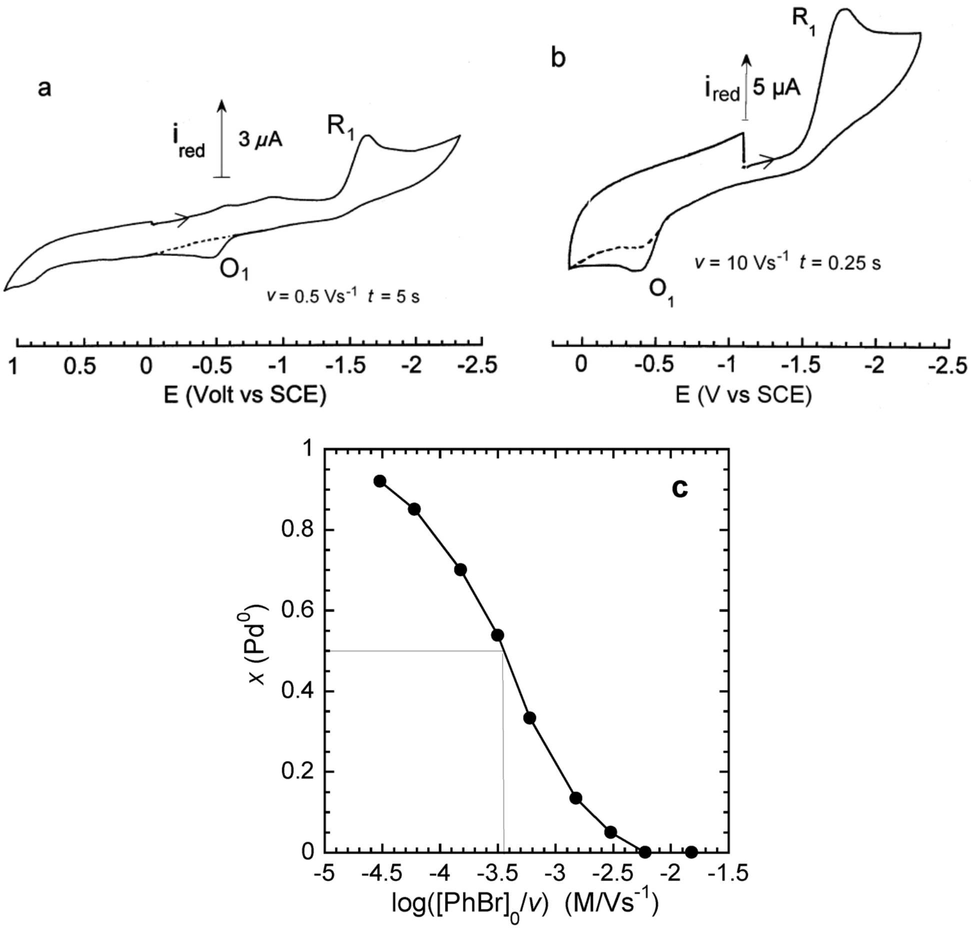


Fig. 2 (—) Reduction of $PdI_2(NHC_{Bn})_2$ (3 mM) in DMF (containing $n\mathrm{Bu}_4\mathrm{NBF}_4$, 0.3 M) at a steady gold disk electrode (d = 0.5 mm) at 20 °C; (- - -) in the presence of PhBr (3 mM): (a) with a scan rate $v = 0.5$ V s^{-1}; (b) with a scan rate $v = 10$ V s^{-1}. (c) Kinetics of the oxidative addition of PhBr (3 mM) to $Pd^0(NHC_{Bn})_2$ (3 mM) generated by the reduction of $PdI_2(NHC_{Bn})_2$ (3 mM) in DMF at 20 °C: plot of the molar fraction x of the unreacted $Pd^0(NHC_{Bn})_2$ vs. $\log([PhBr]_0/v)$.

For each scan rate v, the molar fraction x of $Pd^0(NHC_{Bn})_2$ is given by the ratio of the oxidation peak current at O_1 in the presence of PhBr relative to the oxidation peak current at O_1 in the absence of PhBr. The plot of x vs. $\log([PhBr]_0/v)$ gives the kinetics curve displayed in Fig. 2c. At short times (high scan rates), most $Pd^0(NHC_{Bn})_2$ is still in the diffusion layer (left part of the curve). At longer times (lower scan rates), the amount of $Pd^0(NHC_{Bn})_2$ decreases because it has more and more time to react in the oxidative addition to PhBr. The curve in Fig 2c characterizes a first-order reaction for both $Pd^0(NHC_{Bn})_2$ and PhBr. The value of the rate constant k of the oxidative addition is calculated from the curve in Fig 2c, which provides the value of the scan rate $v_{1/2}$ corresponding to the half-reaction. From the half-reaction time $t_{1/2} = \Delta E/v_{1/2}$ ($\Delta E = (|E^p_{inversion}| - |E^p_{R1}|) + (|E^p_{inversion}| - |E^p_{O1}|)$, k is calculated via the kinetic law: $1/x = kC_0t + 1$. From the value of $k = 1180\ M^{-1}\ s^{-1}$ (Table 2), one sees that the oxidative addition of PhBr is a very fast reaction. The electrochemistry is the only technique that both allows the generation of a transient very reactive species and the characterization of its reactivity by the determination of the rate constant of the oxidative addition.

Table 2 Rate constants k of the oxidative addition of aryl halides to electrogenerated Pd^0 complexes in DMF at 20 °C.

Pd^0 complex	k (M^{-1} s^{-1})				
	PhI	PhBr	PhCl	4-CH_3–C_6H_4–Cl	4-CF_3–C_6H_4–Cl
$Pd^0(NHC_{Bn})_2$	>1180	1180	0.13	0.02	0.35
$Pd^0(NHC_{Bn})(PPh_3)$	830	2	n.d.	n.d.	n.d.

n.d.: not determined

The rate constants of the oxidative addition of $Pd^0(NHC_{Bn})_2$ to aryl halides are gathered in Table 2. The classical reactivity orders are observed [10,12]:

PhI > PhBr > PhCl

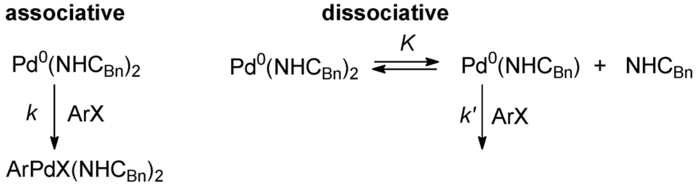
4-CF_3–C_6H_4–Cl > C_6H_5–Cl > 4-CH_3–C_6H_4–Cl

The mixed complex $Pd^0(NHC_{Bn})(PPh_3)$ is less reactive than $Pd^0(NHC_{Bn})_2$ (Table 2). Kinetic data on the reactivity of $Pd^0(NHC_{Bn})_2$ and $Pd^0(NHC_{Bn})(PPh_3)$ with PhI and PhBr were published in early 2003 [10]. This was the first paper on the reactivity of Pd^0 complexes ligated by NHC in oxidative addition to aryl halides. At that time, an associative mechanism was proposed involving $Pd^0(NHC_{Bn})_2$ as the reactive species (Scheme 4). In the late 2003, Caddick, Cloke et al. published a paper on the reactivity of the isolated $Pd^0(NHC_{tBu})_2$ with aryl chlorides [11]. A dissociative mechanism was established involving $Pd^0(NHC_{tBu})$ as the reactive species (vide infra). The mechanism of the oxidative addition of $Pd^0(NHC_{Bn})_2$ was then investigated in more detail [12].

Associative vs. dissociative oxidative addition

Oxidative addition of $Pd^0(NHC_{Bn})_2$

One main way to discriminate between an associative and a dissociative mechanism (Scheme 5) is to test the effect of added NHC on the kinetics of the oxidative addition. If the rate of the oxidative addition is not affected by the concentration of NHC, the mechanism is associative. The mechanism will be dissociative if the reaction is slower in the presence of excess NHC with a reaction order of –1. This strategy cannot be used in the case of NHC_{Bn} because the latter cannot be isolated [10].



Scheme 5 Putative mechanisms for the oxidative addition of $Pd^0(NHC_{Bn})_2$.

The problem is solved via the investigation of the mechanism of the oxidative addition of the mixed complex $Pd^0(NHC_{Bn})(PPh_3)$ [12]. Firstly, it is observed that PPh_3 cannot displace NHC_{Bn} from $Pd^0(NHC_{Bn})(PPh_3)$ (eq. 1 in Scheme 6). Indeed, the well-known oxidation peak of $Pd^0(PPh_3)_3$ [17b] (see Table 1) is never observed when $PdI_2(NHC_{Bn})_2$ is reduced in the presence of a large excess of PPh_3 (up to 10 equiv) in DMF. Consequently, the affinity of NHC_{Bn} for Pd^0 is higher than that of PPh_3 [18] and the dissociation of NHC_{Bn} is not favored (eq. 2 in Scheme 6).

$$\mathrm{Pd^0(NHC_{Bn})(PPh_3)} + \mathrm{PPh_3} \nrightarrow \mathrm{Pd^0(PPh_3)_{n\,=\,2\;or\;3}} + \mathrm{NHC_{Bn}} \quad (1)$$

$$\mathrm{Pd^0(NHC_{Bn})(PPh_3)} \not\rightleftarrows \mathrm{Pd^0(PPh_3)} + \mathrm{NHC_{Bn}} \quad (2)$$

Scheme 6 Unfavored dissociative pathway from the mixed complex $Pd^0(NHC_{Bn})(PPh_3)$.

The second way of dissociation of $Pd^0(NHC_{Bn})(PPh_3)$ would be the dissociation of PPh_3 (eq. 3 in Scheme 7). If the oxidative addition of $Pd^0(NHC_{Bn})(PPh_3)$ proceeded in a dissociative mechanism via $Pd^0(NHC_{Bn})$, the reaction should be slower in the presence of excess PPh_3. But no decelerating effect of PPh_3 is observed in the reaction of $Pd^0(NHC_{Bn})(PPh_3)$ with PhI or PhCl. Consequently, $Pd^0(NHC_{Bn})(PPh_3)$ is the reactive species in a pure associative mechanism [12] (Scheme 7).

$$\begin{tikzcd} \mathrm{Pd^0(NHC_{Bn})(PPh_3)} \arrow[r, phantom, "\not\rightleftarrows"] \arrow[d, "k"', "\mathrm{ArX}"] & \mathrm{Pd^0(NHC_{Bn})} + \mathrm{PPh_3} \quad (3) \\ \mathrm{ArPdX(NHC_{Bn})(PPh_3)} & \end{tikzcd}$$

$$\begin{tikzcd} \mathrm{Pd^0(NHC_{Bn})_2} \arrow[r, phantom, "\not\rightleftarrows"] \arrow[d, "k"', "\mathrm{ArX}"] & \mathrm{Pd^0(NHC_{Bn})} + \mathrm{NHC_{Bn}} \quad (4) \\ \mathrm{ArPdX(NHC_{Bn})_2} & \end{tikzcd}$$

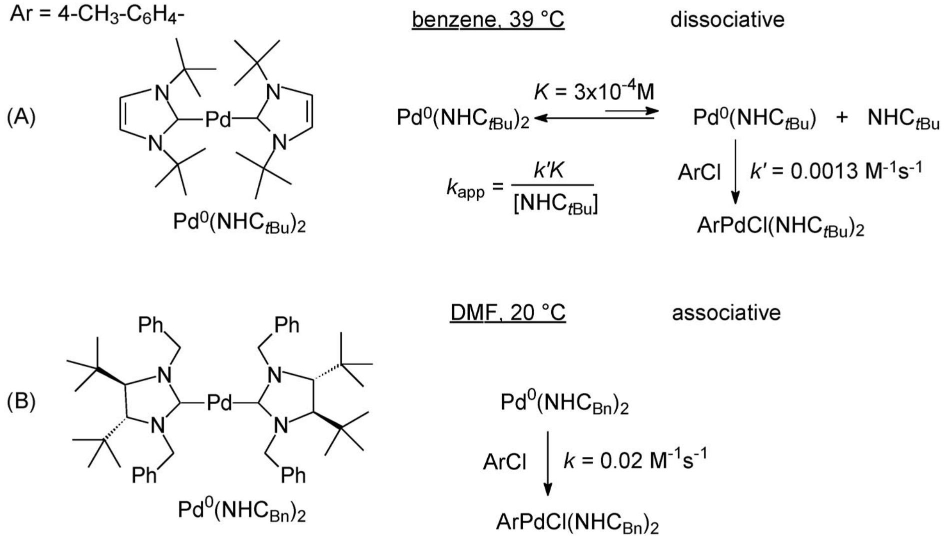
Scheme 7 Established associative mechanisms for $Pd^0(NHC_{Bn})(PPh_3)$ and $Pd^0(NHC_{Bn})_2$.

If the oxidative addition of $Pd^0(NHC_{Bn})_2$ proceeded in a dissociative mechanism via $Pd^0(NHC_{Bn})$, the concentration of $Pd^0(NHC_{Bn})$ in the equilibrium of eq. 4 in Scheme 7, should be lower than that in the equilibrium in eq. 3 because NHC_{Bn} is a better ligand for $Pd^0(NHC_{Bn})$ than PPh_3 (vide supra). Consequently, $Pd^0(NHC_{Bn})_2$ should be less reactive (via $Pd^0(NHC_{Bn})$ than $Pd^0(NHC_{Bn})(PPh_3)$. The reverse situation is observed: $Pd^0(NHC_{Bn})_2$ is more reactive than $Pd^0(NHC_{Bn})(PPh_3)$ (Table 2). Consequently, $Pd^0(NHC_{Bn})_2$ is the reactive species in a pure associative mechanism [12] (Scheme 7). $Pd^0(NHC_{Bn})_2$ is more reactive than $Pd^0(NHC_{Bn})(PPh_3)$ because it is more electron-rich.

Comparative oxidative addition of $Pd^0(NHC_{Bn})_2$ and $Pd^0(NHC_{tBu})_2$ to aryl chlorides

Caddick, Cloke et al. have established that the isolated bis-carbene $Pd^0(NHC_{tBu})_2$ [14] does not directly react with aryl chlorides in an associative mechanism but via the monocarbene $Pd^0(NHC_{tBu})$ in a dissociative mechanism [11] (path A in Scheme 8). The oxidative addition is indeed slower in the presence of NHC_{tBu} (a stable carbene) [19] with a reaction order of –1. NHC_{tBu} is stable because of the two bulky *t*butyl groups on the N atoms. Due to the bulk of the ligand, $Pd^0(NHC_{tBu})_2$ is prone to dissociate to $Pd^0(NHC_{tBu})$ and NHC_{tBu}. The oxidative addition to *para*-chlorotoluene has been followed by ^1H NMR in benzene at 39 °C. The reaction is quite slow because the reactive mono-carbene $Pd^0(NHC_{tBu})$ is generated at very low concentration in its equilibrium with the major nonreactive bis-carbene $Pd^0(NHC_{tBu})_2$. The reaction is characterized by an apparent rate constant $k_{app} = k'K/[NHC_{tBu}]$ (path A in Scheme 8).

In contrast, NHC_{Bn} is less bulky than NHC_{tBu}, $Pd^0(NHC_{Bn})_2$ does not dissociate and is the reactive species (path B in Scheme 8). Even if the reaction is performed at a lower temperature (20 vs. 39 °C), the electrogenerated $Pd^0(NHC_{Bn})_2$ is more reactive with *para*-chlorotoluene than



Scheme 8 Comparative mechanisms for the oxidative addition of $Pd^0(NHC_{tBu})$ and $Pd^0(NHC_{Bn})_2$.

$Pd^0(NHC_{tBu})_2$ at identical concentrations [11,12]. Consequently, at identical concentrations, a bis-carbene Pd^0 complex such as $Pd^0(NHC_{Bn})_2$, which reacts in an associative mechanism, may be more reactive than a bis-carbene Pd^0 complex such as $Pd^0(NHC_{tBu})_2$, which reacts via $Pd^0(NHC_{tBu})$ in a dissociative mechanism because the latter complex is always present at very low concentration.

$$Pd^0(NHC_{Bn})_2 \; > \; Pd^0(NHC_{tBu}) \; >> \; \underset{\text{unreactive}}{Pd^0(NHC_{tBu})_2}$$

Linear Pd^0L_2 (L-Pd-L) complexes must be bent to undergo oxidative addition [20]. There is no steric demand around the Pd center in $Pd^0(NHC_{Bn})_2$, which can easily be bent prior oxidative addition. In contrast, there is a strong steric hindrance in $Pd^0(NHC_{tBu})_2$, which cannot be bent and cannot react as it. Instead, a dissociation of the bulky ligand NHC_{tBu} takes place.

Therefore, the structure of the reactive species in oxidative additions, a bis- or a mono-carbene Pd^0 complex, seems to be controlled by the bulk of the NHC ligand. However, there is no relationship between the structure of the reactive species and its reactivity since for two different carbenes, the bis-carbene $Pd^0(NHC_{Bn})_2$ can be even more reactive than the mono-carbene $Pd^0(NHC_{tBu})$ when generated at the same concentration (compare respective values of k and k' in Scheme 8). Therefore, having in hand a reactive mono-carbene Pd^0 complex is not a guarantee for a fast oxidative addition because it is always generated at low concentration in its equilibrium with the related nonreactive bis-carbene Pd^0 complex.

CONCLUSION

Electrochemistry is an efficient technique that can mimic the chemical reduction of Pd^{II} precursors ligated by NHCs to generate bis-carbene Pd^0 complexes, $Pd^0(NHC)_2$. Moreover, kinetic data on the reactivity of $Pd^0(NHC)_2$ complexes in oxidative additions to aryl bromides and chlorides can be obtained by the same technique. $Pd^0(NHC_{Bn})_2$ is found to be more reactive than the mixed complex $Pd^0(NHC_{Bn})(PPh_3)$. Both are the reactive species in an associative mechanism. In the case of more bulky ligands such as NHC_{tBu}, the isolated bis-carbene $Pd^0(NHC_{tBu})_2$ dissociates to the mono-carbene $Pd^0(NHC_{tBu})$, which is the reactive species in oxidative additions to aryl chlorides. The reactivity of the mono-carbene $Pd^0(NHC_{tBu})$ is, however, controlled and limited by its low concentration in its equilibrium with the major but unreactive bis-carbene $Pd^0(NHC_{tBu})_2$.

ACKNOWLEDGMENTS

We thank CNRS, ENS (MNRT), and the Université Pierre et Marie Curie for financial support.

REFERENCES AND NOTES

1. (a) J. F. Fauvarque, F. Pflüger, M. Troupel. *J. Organomet. Chem.* **208**, 419 (1981); (b) C. Amatore, F. Pflüger. *Organometallics* **9**, 2276 (1990); (c) C. Amatore, A. Jutand, F. Khalil, M. A. M'Barki, L. Mottier. *Organometallics* **12**, 3168 (1993).
2. For $Pd^0(PPh_3)_3$ generated as the major complex from $Pd^0(PPh_3)_4$, see: (a) B. E. Mann, A. Musco. *J. Chem. Soc., Dalton Trans.* 1673 (1975); (b) J. Evans, L. O'Neill, V. L. Kambhampati, G. Rayner, S. Turin, A. Genge, A. J. Dent, T. Neisius. *J. Chem. Soc., Dalton Trans.* 2207 (2002).
3. Reaction rate = $k[Pd^0L_2][ArX] = kK[Pd^0L_3][ArX]/[L] = k_{app}[Pd^0L_3][ArX]$.
4. A. Jutand, A. Mosleh. *Organometallics* **14**, 1810 (1995).
5. (a) J. F. Hartwig, F. Paul. *J. Am. Chem. Soc.* **117**, 5373 (1995); (b) F. Barrios-Landeros, J. F. Hartwig. *J. Am. Chem. Soc.* **127**, 6944 (2005); (c) F. Barrios-Landeros, B. P. Carrow, J. F. Hartwig. *J. Am. Chem. Soc.* **131**, 8141 (2009).
6. E. Galardon, S. Ramdeehul, J. M. Brown, A. Cowley, K. K. Hii, A. Jutand. *Angew. Chem., Int. Ed.* **41**, 1760 (2002).
7. R. B. Jordan. *Organometallics* **26**, 4763 (2007).
8. W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus. *Angew. Chem., Int. Ed.*, **34**, 2371 (1995).
9. For reviews, see: (a) W. A. Herrmann, C. Köcher. *Angew. Chem., Int. Ed. Engl.* **36**, 2162 (1997); (b) W. A. Herrmann. *Angew. Chem., Int. Ed.* **41**, 1290 (2002); (c) A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang, S. P. Nolan. *J. Organomet. Chem.* **653**, 69 (2002); (d) W. A. Herrmann, K. Öfele, D. V. Preysing, S. Schneider. *J. Organomet. Chem.* **687**, 229 (2003); (e) K. J. Cavell, D. S. McGuinness. *Coord. Chem. Rev.* **248**, 671 (2004); (f) V. Farina. *Adv. Synth. Catal.* **346**, 1553 (2004); (g) N. M. Scott, S. P. Nolan. *Eur. J. Inorg. Chem.* 1815 (2005); (h) F. Alonso, I. P. Beletskaya, M. Yus. *Tetrahedron* **61**, 11771 (2005); (i) F. Alonso, I. P. Beletskaya, M. Yus. *Tetrahedron* **64**, 3047 (2008).
10. J. Pytkowicz, S. Roland, P. Mangeney, G. Meyer, A. Jutand. *J. Organomet. Chem.* **678**, 166 (2003).
11. A. K. de K. Lewis, S. Caddick, F. G. N. Cloke, N. C. Billingham, P. B. Hitchcock, J. Leonard. *J. Am. Chem. Soc.* **125**, 10066 (2003).
12. S. Roland, P. Mangeney, A. Jutand. *Synlett* 3088 (2006).
13. D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand. *Chem. Rev.* **100**, 39 (2000).
14. P. L. Arnold, F. G. N. Cloke, T. Geldbach, P. B. Hitchcock. *Organometallics* **18**, 3228 (1999).
15. For a review on the use of electrochemistry to solve mechanistic problems in transition-metal-catalyzed reactions, see: A. Jutand. *Chem. Rev.* **108**, 2300 (2008).
16. For the technique used to determine the absolute number n of electron(s) involved in any electrochemical process, see ref. [15] and: C. Amatore, M. Azzabi, P. Calas, A. Jutand, C. Lefrou, Y. Rollin. *J. Electroanal. Chem.* **288**, 45 (1990).
17. (a) A. Jutand, A. Mosleh. *J. Org. Chem.* **62**, 261 (1997); (b) C. Amatore, A. Jutand, F. Khalil, M. A. M'Barki, L. Mottier. *Organometallics* **12**, 3168 (1993).

18. In agreement with: (a) R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan. *J. Am. Chem. Soc.* **127**, 2485 (2005); (b) S. Diez-Gonzalez, S. P. Nolan. *Coord. Chem. Rev.* **251**, 874 (2007).
19. A. J. Arduengo III, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, R. West. *J. Am. Chem. Soc.* **116**, 6641 (1994).
20. S. Kozuch, S. Shaik, A. Jutand, C. Amatore. *Chem.—Eur. J.* **10**, 3072 (2004).