Oxidative Addition of Aryl Halides to Transient Anionic σ-Aryl–Palladium(0) Intermediates—Application to Palladium-Catalyzed Reductive Coupling of Aryl Halides

Christian Amatore,* Emmanuelle Carré, Anny Jutand,* Hideo Tanaka, Qinghua Ren, and Sigeru Torii*

Abstract: The rates and mechanism of the reactions of a series of aryl-ligated, anionic palladium(0) complexes $Ar-Pd^0(PPh_3)_2^-$ with *para*-substituted iodobenzenes were investigated by means of transient electrochemistry. The reaction was found to be first order in each reactant and to proceed similarly to oxidative addition of aryl halides to the halide-ligated species $X-Pd^0(PPh_3)_2^-$, although much faster and less sensitive to electronic factors. Owing to the short lifetime ($t_{1/2} \approx$ 1–5 ms) of the product of this reaction, it could not be characterized in detail. However, based on kinetic results, this transient species is thought to be an anionic pentacoordinated bisarylpalladium(II) complex, which undergoes rapid loss of halide ligand to yield, most probably, a bisarylpalladium(II) neutral species. Based on the study of this reaction and on previously reported results, we propose a mechanism for the palladium-catalyzed homocoupling of aryl halides consisting of a catalytic cycle initiated by oxidative addition of an aryl halide to a zerovalent tris-ligated palladium center. Two-electron reduction of the pentacoordinated arylpalladium(II) anionic species thus formed gives a tris-ligated anionic arylpalladium(0) center, which undergoes oxidative addition with a second aryl halide molecule to eventually lead to a bisarylpalladium(II) neutral species. Reductive elimination of a bisaryl molecule from this center closes the catalytic cycle by regenerating the initial zerovalent palladium complex. The application of this sequence to the catalytic heterocoupling of aryl halides is discussed, and it is concluded, on the basis of Hammett correlations, that statistical yields should be observed, in agreement with the results obtained for preparative reactions in DMF.

Keywords
catalysis · C–C coupling · mechanistic studies · oxidative addition · palladium complexes

Introduction

Zerovalent d^{10} transition metal complexes are known to be efficient catalysts. Under classical homogeneous conditions, two main procedures are usually used for the homo- and cross-coupling reactions of aromatic halides or pseudo-halides. In the first procedure, one aromatic halide species is used as is, while the second one is first converted into an organometallic reagent [Eq. (1), M′ = MgX, ZnX, Li, etc.].[1, 2] The overall reaction [Eq. (2)] is therefore a transition metal catalyzed nucleophilic

$$ArX \longrightarrow ArM' \quad (1)$$

$$Ar'X' + ArM \xrightarrow{M^0L_n} Ar-Ar' + M'X' \quad (2)$$

substitution. Since each halide has a different function (i.e., substrate vs. nucleophile) excellent yields of unsymmetrical biaryls may be obtained by this procedure. Palladium(0) complexes have been shown to be very efficient catalysts in these reactions.[1b, 3]

The second procedure that can be used is based the seminal work of Semmelhack et al.,[4] modified and improved by Kumada and co-workers.[5a] It involves the direct reaction of two aryl halides, with the reductive driving force of the reaction being provided by a stoichiometric amount of a reducing metal powder [Eq. (3), M′ = Zn].[5] This method has been further adapted by replacing the reducing metal powder by a cathode [Eq. (4)].[6] This electrochemical procedure is generally very

$$2ArX + M' \xrightarrow{M^0L_n} Ar-Ar + M'X_2 \quad (3)$$

$$2ArX + 2e^- \xrightarrow{M^0L_n} Ar-Ar + 2X^- \quad (4)$$

convenient for the homocoupling of functionalized aryl halides, since it does not require the use of stoichiometric quantities of an organometallic reagent and is therefore expected to be compatible with a range of substituents at the aryl moiety. The most widely used catalysts in Equations (3) and (4) are nickel(0)-centered complexes,[4–6] and the mechanism under these conditions was established several years ago.[6] The catalytic chain was shown to proceed along a sequence that involves alternating diamagnetic and paramagnetic nickel-centered complexes. We

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wish to show here that palladium catalysis of reaction (4) proceeds along a completely different route and involves only diamagnetic palladium-centered species.

Results and Discussion

Some of us have established previously that activation of arylpalladium(II) complexes by electron transfer proceeds through an overall two-electron reduction,[7a] instead of the one-electron sequences found for the corresponding nickel species (Ar–Ni^{II}Xdppe, dppe = 1,2-bis(diphenylphosphino)ethane).[6] A tris-ligated anionic arylpalladium(0) intermediate is thus formed [Eq. (5)],[7a] which is the formal equivalent to $X{-}Pd^0L_2^-$

$$Ar{-}Pd^{II}XL_2 + 2e^- \longrightarrow Ar{-}Pd^0L_2^- + X^- \qquad (5)$$

(X = Br, Cl),[8] the halide-ligated anionic zerovalent palladium complex generated upon two-electron reduction of the stable dihalide palladium(II) precursor $Pd^{II}X_2L_2$. In the absence of added aryl halide and with a *para*-substituted phenyl moiety Ar, $Ar{-}Pd^0L_2^-$ was shown to reversibly give a neutral zerovalent palladium center and a σ-aryl anion [Eq. (6)], which could then react with a suitable electrophile present in the medium (e.g., acid, CO_2, acidic impurities, etc.) [Eq. (7)].[7a, b] Note that in

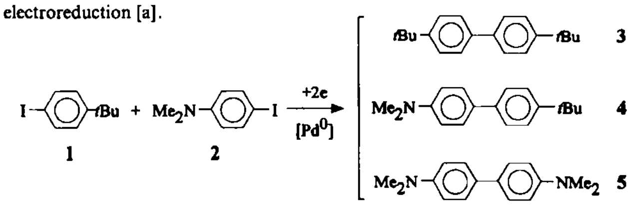
$$Ar{-}Pd^0L_2^- \rightleftharpoons Ar^- + Pd^0L_2 \qquad (6)$$

$$Ar^- + E^+ \longrightarrow Ar{-}E \qquad (7)$$

Equation (6) as well as in the following, the zerovalent species formed is written Pd^0L_2 for convenience and simplicity, although this unsaturated species is actually rapidly ligated by one or more solvent molecules or by the halide ion expelled in reaction (5).[8]

The mechanism outlined above was shown to describe accurately the palladium-catalyzed electrocarboxylation of aryl halides ($E^+ = CO_2$).[7a] However, it is extremely unlikely that it applies to homo- or heterocoupling reactions, since aryl halides are known to be poor electrophiles, except when they are stabilized by strong electron-withdrawing groups (vide infra). On the other hand, some of us have already established that palladium complexes are efficient catalysts of homocoupling reactions (Table 1, entries 1–2).[9] This apparent contradiction prompted us to investigate the detailed reactivity of $Ar{-}Pd^0L_2^-$ in the presence of aryl halides and examine its potential in heterocoupling reactions.

Table 1. Palladium-catalyzed homo- and heterocoupling of aryl iodides by cathodic electroreduction [a].



	Conditions [b,c]					Yields [d]/mmol (%)		
Proc.	1	2	$PdCl_2(PPh_3)_2$	PPh_3	*Q*/C	3	4	5
A	0.3	–	0.02	0.04	106	0.145 (97)	–	–
A	–	0.3	0.02	0.04	135	–	–	0.14 (92)
A	0.3	0.3	0.02	0.04	95	0.065 (21)	0.135 (45)	0.073 (24)
B	0.3	0.3	0.3	0.6	67 +95	0.025 (8)	0.23 (76)	0.033 (11)

[a] Constant current electrolysis (7.5 mA; 2.5 mA cm^{-2}). Divided cell. Cathodic compartment: 5 mL DMF +0.5 g Et_4NOTs; lead cathode (1.5 × 2 cm^2 sheet). Anodic compartment: 5 mL DMF +0.5 g Et_4NOTs; platinum anode (1.5 × 2 cm^2 sheet). [b] The results reported in the first two rows of Table 1 have already been reported in ref. [9], but were repeated in the present study to ensure a meaningful comparison with the other results (two last rows). *Procedure A*: The cathodic compartment was charged with the (or both) aryl halide(s), the palladium catalyst, and the phosphine, and then current was applied (see Experimental Section). *Procedure B*: The cathodic compartment was charged with stoichiometric amounts of the palladium complex and phosphine, and current was then applied; after 67 C (2.2 F mol^{-1}), electrolysis was interrupted, and **2** was added to the catholyte and left to react for 0.5 h with stirring; **1** was then added and an additional 95 C were passed (see Experimental Section). [c] Quantities given in mmol, and charge passed (Q) in coulombs. [d] Isolated yields in mmol (and as a % at 100% conversion).

Mechanism Based on Cyclic Voltammetry: In the absence of added aryl halide, the voltammetric reduction of authentic samples of $Ar{-}Pd^{II}XL_2$ (L = monodentate phosphine ligand) proceeds through an overall two-electron ($n = 2.2 \pm 0.2$)[7a] wave R_1 (Table 2; compare Fig. 1a for Ar = 2-C_4H_3S, X = I, L = PPh_3) to afford the corresponding $Ar{-}Pd^0L_2^-$ anionic complex as primary reduction product [Eq. (5)]. Evidence for the formation of this species is provided by its oxidation wave O_2,[7a, b] which is observed on scan reversal.[10a] The addition of aryl halides to the solution does not affect the peak potential nor the peak current of wave R_1. The oxidation wave O_2 due to the anionic zerovalent arylpalladium(0) products, $Ar{-}Pd^0L_2^-$, continues to be observed with an identical current magnitude on the return scan provided that the voltammetry is performed at a

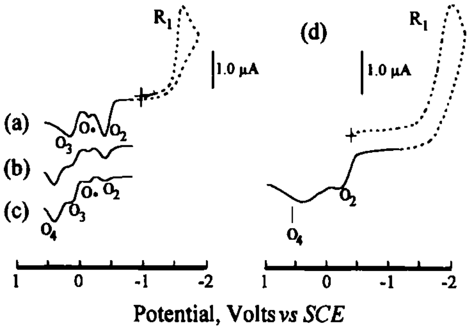


Fig. 1. a–c) Cyclic voltammetry ($v = 0.5\ Vs^{-1}$) of 2-thienyl–$Pd^{II}I(PPh_3)_2$, 2 mM in THF, 0.3 M NBu_4BF_4, gold disk electrode (diameter 0.5 mm), 20 °C: a) no additional reagent, b) in the presence of 2 mM PhI, and c) in the presence of 2 mM PhI and 2 mM PPh_3. d) Same as (c) but at $v = 100\ Vs^{-1}$ and at a 0.125 mm diameter gold disk electrode. Note that a different current scale is used for the cathodic and anodic sections of all voltammograms to facilitate the examination of the anodic sections: × 1 (cathodic sections, dashed curves) or background subtracted, and × 4 (anodic sections, solid curves) with respect to the scale indicated on each panel; also in (b,c) only the anodic sections of the voltammograms are shown, since the cathodic parts are identical to that shown in (a).

Table 2. Peak potentials of the various waves observed during cyclic voltammetry of several arylpalladium(II) complexes ($Ar{-}Pd^{II}X(PPh_3)_2$) and aryl halides (ArX) examined in this study [a].

Ar	X	$E^p(R_1)$ [b]	$E^p(R_2)$ [c]	$E^p(O_2)$ [d]	$E^p(O_3)$ [e]	$E^p(O^*)$ [f]
2-C_4H_3S	Br	−1.80	−2.20	–	–	–
	I	−1.70	−1.25	−0.39 (−0.27)	0.10	−0.14
C_6H_5	Cl	−2.04	< −2.80	(−0.45)	0.14 (0.27)	none
	Br	−2.01	−2.80	(−0.44)	0.14 (0.28)	none
	I	−1.92	−2.20	(−0.42)	0.15 (0.28)	none
4-CN-C_6H_4	Br	−1.82	–	−0.20 (−0.38)	0.11 (0.23)	none
4-CH_3-C_6H_4	I	−2.00	−2.40	(−0.47)	(0.23)	none

[a] In THF, 0.3 M NBu_4BF_4, at a gold disk electrode (0.5 mm diameter), 20 °C. Values of peak potentials are given in V vs. SCE (error ±10 mV) measured at 0.2 Vs^{-1} or at 100 Vs^{-1} (values given in parentheses). Peak potentials of the iodide ion oxidation wave at 0.2 Vs^{-1}: 0.40 V vs. SCE (wave O_4). [b] Reduction wave of $Ar{-}Pd^{II}X(PPh_3)_2$. [c] Reduction wave of ArX. [d] Oxidation wave of $Ar{-}Pd^0(PPh_3)_2^-$. [e] Oxidation wave of "$Pd^0(PPh_3)_2$" centers [8d]. [f] Oxidation wave of the σ-aryl anion Ar^-.

sufficiently high scan rate ($v > 500\ \mathrm{Vs^{-1}}$). All these features demonstrate that aryl halides do not interfere in the primary reduction mechanism of $\mathrm{Ar{-}Pd^{II}XL_2}$, which still proceeds to the anionic species $\mathrm{Ar{-}Pd^0L_2^-}$ [Eq. (5)]. In particular, this stresses that the homocoupling products reported in the two first entries[9] of Table 1 cannot be formed in a sequence initiated by the fast interception by the aryl halide of a short-lived arylpalladium(I)[11] intermediate formed by an EE or ECE sequence (E: electron transfer, C: chemical reaction; Scheme 1).[12] In other words, the above voltammetric results establish that any reaction with the second aryl halide molecule necessarily occurs with $\mathrm{Ar{-}Pd^0L_2^-}$ or with one of its follow-up products.

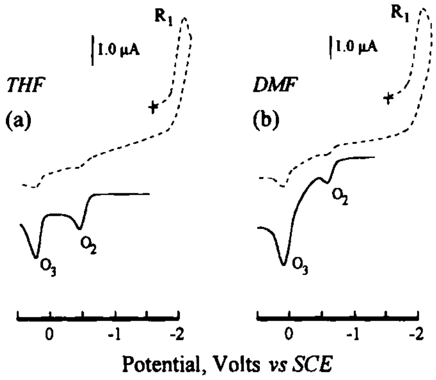
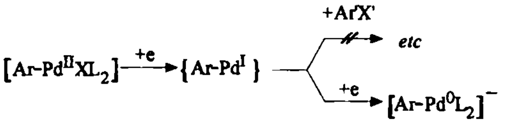


Fig. 2. Cyclic voltammetry of $\mathrm{C_6H_5{-}Pd^{II}Br(PPh_3)_2}$ (2 mM) in a) THF, 0.3 M $\mathrm{NBu_4BF_4}$ and b) DMF, 0.3 M $\mathrm{NBu_4BF_4}$. Gold disk electrode (diameter 0.125 mm), $v = 100\ \mathrm{Vs^{-1}}$, 20 °C. The solid curves correspond to the anodic sections of the voltammograms after background subtraction and enlargement of the current scales (×4 in (a) and ×3 in (b) with respect to the scale indicated on each panel) to facilitate the examination of the anodic sections of each voltammogram.



Scheme 1.

At lower scan rates, wave $\mathrm{O_2}$ is still observable in the presence of an added aryl halide, yet its current peak is smaller than in the absence of an electrophile (Fig. 1 b). Wave $\mathrm{O_3}$, which corresponds to the oxidation of the low-coordinate zerovalent species $\mathrm{Pd^0L_2}$ formed upon dissociation of the aryl anion from $\mathrm{Ar{-}Pd^0L_2^-}$ [Eq. (6)],[7b] also decays in the presence of an aryl halide (Fig. 1 b). This is in complete agreement with the observation that low-coordinate species $\mathrm{Pd^0L_2}$ react extremely fast with aryl halides [Eq. (8)].[8, 10b] In DMF, which is the second solvent

$$\mathrm{Pd^0L_2 + ArX \longrightarrow Ar{-}Pd^{II}XL_2} \qquad (8)$$

considered in this study essentially identical results are obtained, especially for preparative scale experiments. However, at slow scan rates reduction of $\mathrm{Ar{-}Pd^{II}XL_2}$ does not proceed only through wave $\mathrm{R_1}$ (Eq. (5); $E^p = -1.95$ V vs. SCE at $0.2\ \mathrm{Vs^{-1}}$ for Ar = Ph, X = Br, and L = $\mathrm{PPh_3}$ in DMF) as is the case in THF, but also occurs concurrently at less negative potentials (wave $\mathrm{R'_1}$; $E^p = -1.75$ V vs. SCE at $0.2\ \mathrm{Vs^{-1}}$ for Ar = Ph, X = Br and L = $\mathrm{PPh_3}$) through a CE mechanism involving the endergonic formation of a transient cationic species [Eq. (9)].[13]

$$\mathrm{Ar{-}Pd^{II}XL_2 \underset{+X^-}{\overset{-X^-}{\rightleftharpoons}} Ar{-}Pd^{II}L_2^+} \qquad (9)$$

At high scan rates, despite the process in Equation (9), the same anionic species as in THF are produced, as shown by the presence of their oxidation waves $\mathrm{O_2}$ and $\mathrm{O_3}$ (Fig. 2b; $E^p = -0.64$ and $+0.09$ V vs. SCE for waves $\mathrm{O_2}$ and $\mathrm{O_3}$, respectively, at $100\ \mathrm{Vs^{-1}}$ in DMF). Because of the additional scan rate dependent[8b] kinetic complication due to the process in Equation (9) occurring in DMF, and, most importantly, because of the difficulty of performing precise measurements in DMF in the potential range of interest (compare the residual background contribution in Fig. 2a and b in the potential range -0.1–0.4 V vs. SCE), we decided to perform the present kinetic analysis in THF.

We have established previously that, when Ar is a phenyl ligand, reaction (6) is a fast equilibrium.[7a] Despite the existence of a fast equilibrium of this type between $\mathrm{Ar{-}Pd^0L_2^-}$ (wave $\mathrm{O_2}$ in Fig. 1 for Ar = 2-thienyl) and $\mathrm{Pd^0L_2}$ (wave $\mathrm{O_3}$ in Fig. 1), two distinct waves (namely, $\mathrm{O_2}$ and $\mathrm{O_3}$) could be observed in previous[7a, b] and in the present investigations, because all the aryl anions formed in reaction (6) are consumed by reaction with the medium (e.g., reaction (7)) while the potential is spanned between peaks $\mathrm{R_1}$ and $\mathrm{O_2}$. This precludes the oxidation of all zerovalent palladium centers at wave $\mathrm{O_2}$ by displacement of equilibrium (6);[7b] thus, the two distincts waves $\mathrm{O_2}$ ($\mathrm{Ar{-}Pd^0L_2^-}$) and $\mathrm{O_3}$ ($\mathrm{Pd^0L_2}$) are observed. In other words, reaction (6) behaves kinetically as a fast preequilibrium for any of the homogeneous processes that occur during the voltammetric scan between waves $\mathrm{R_1}$ and $\mathrm{O_2}$ (e.g., reactions such as that in Eq. (7) or any other possible reactions involving $\mathrm{Ar{-}Pd^0L_2^-}$ or $\mathrm{Pd^0L_2}$, such as reaction (8), vide infra), and yet it can be considered as an irreversible reaction as far as the electrochemical detection of $\mathrm{Ar{-}Pd^0L_2^-}$ or $\mathrm{Pd^0L_2}$ is concerned, and it does not give rise to a CE electrochemical sequence.[8] This has been established quantitatively in previous work for phenyl ligands,[7a] and is therefore valid for most of the kinetic situations considered here.

When Ar is a 2-thienyl ligand (Fig. 1, Ar = Th), owing to the greater stability of the 2-thienyl anion, not all of it is consumed while the potential is spanned between peaks $\mathrm{R_1}$ and $\mathrm{O_2}$. Evidence for this is provided by the observation of an oxidation wave (O* in Fig. 1a–c) for this species. The presence of three distinct waves for $\mathrm{Th{-}Pd^0L_2^-}$ ($\mathrm{O_2}$), $\mathrm{Th^-}$ (O*), and $\mathrm{Pd^0L_2}$ ($\mathrm{O_3}$) suggests that the backward reaction (6) is slower than in the case of phenyl ligands. Again this may be ascribed to the fact that the 2-thienyl anion is more stable than the σ-phenyl anion. However, since the size of wave O* is too small to allow precise kinetic measurements, it is impossible to decide at this level whether reaction (6) can be considered to be completely irreversible or whether it possesses some degree of reversibility that may give rise to a partial involvement of a CE mechanism at the level of wave $\mathrm{O_2}$. However, based on the well-defined peaked shape of wave $\mathrm{O_2}$,[8b] such a CE contribution to the oxidation current at wave $\mathrm{O_2}$, if any, is necessarily much smaller than the direct oxidation current. We can then safely conclude that in both cases investigated here (Ar = phenyl or thienyl) the oxidation current at wave $\mathrm{O_2}$ reflects the homogeneous concentration of $\mathrm{Ar{-}Pd^0L_2^-}$ in the diffusion layer and is not perceptibly distorted by a CE mechanism. As far as the electrochemical detection of $\mathrm{Ar{-}Pd^0L_2^-}$ is concerned, the situation is then identical to that observed in our previous work.[7a]

Despite the fact that the effect of the backward reaction in Equation (6) is negligible in our electrochemical detection, it may play a significant role in determining the actual concentration of $\mathrm{Ar{-}Pd^0L_2^-}$ in the diffusion layer. Indeed, electrochemically formed $Ar-Pd^0L_2^-$ reacts homogeneously while the potential scan is spanned between waves R_1 (where $Ar-Pd^0L_2^-$ is formed) and O_2 (where $Ar-Pd^0L_2^-$ is detected). When reaction (6) is irreversible, any possible reaction with Ar^- or Pd^0L_2 does not affect the kinetics of $Ar-Pd^0L_2^-$ evolution, which then obeys first-order kinetics with a rate constant equal to that of the forward reaction in Equation (6). Conversely, when reaction (6) equilibrates, any follow-up reaction of Ar^- or Pd^0L_2 controls kinetically the concentration of $Ar-Pd^0L_2^-$, owing to the continuous displacement of reaction (6), as we have established previously with aryl ligands.[7a] In other words, the decrease of the peak current of wave O_2, that is, the diminished concentration of $Ar-Pd^0L_2^-$ in the presence of aryl halide, might reflect not only a direct reaction of the added aryl halide with $Ar-Pd^0L_2^-$, but might be biased in part or totally by the involvement of the fast reaction (8)[8a] or of a reaction between the Ar^- anion and the added aryl halide, if any is present. We wish to show below how these possible kinetic biases can be eliminated, to allow the determination of the true reactivity of $Ar-Pd^0L_2^-$ with aryl halides.

Let us first consider the possible involvement of reaction (8), which can be combined with Equation (6) to give Equation (10). Previous studies[8] have established that, in the

$$Ar-Pd^0L_2^- \underset{+Ar^-}{\overset{-Ar^-}{\rightleftharpoons}} Pd^0L_2 \xrightarrow{Ar'X'} Ar'-Pd^{II}X'L_2 \qquad (10)$$

presence of PPh_3, "$Pd^0(PPh_3)_2$" undergoes a rapid exergonic phosphine ligation to afford the much more stable zerovalent complex $Pd^0(PPh_3)_3$, before it reacts with an aryl halide [Eq. (11)].[8a, c, d] The whole sequence in Equation (11) is thus

$$Ar-Pd^0L_2^- \xrightarrow{-Ar^-} Pd^0L_2 \xrightarrow{+L} Pd^0L_3 \qquad (11)$$

forced to behave like an irreversible reaction.[7a] The comparison between Figures 1 b and c, which illustrates the effect of the addition of an equivalent of PPh_3, confirms this conclusion.[8d] It is indeed observed that the peak current of wave O_2 decreases significantly following the addition of the phosphine ligand; this reflects the fact that the irreversible sequence in Equation (11) is much faster than the original reactions in Equation (10); the latter is then necessarily ruled out. Note that this establishes indirectly that, in the absence of phosphine, the fate of Pd^0L_2 plays a tangible kinetic role in determining the overall intrinsic reactivity of $Ar-Pd^0L_2^-$. So, for the 2-thienyl ligand the situation is identical to that of phenyl ligands, for which this has been established more quantitatively;[7] this shows that reaction (6) also possesses some degree of reversibility when Ar = Th. However, any kinetic artifact due to this fact is excluded in the presence of one equivalent of phosphine, since Equation (11) then behaves like a kinetically irreversible sequence; the rate determining step is the cleavage of the aryl ligand (i.e., the forward reaction in Eq. (6)). For this reason all the kinetic experiments performed here are conducted in the presence of one equivalent of triphenylphosphine.

Let us now consider the possibility of a reaction between the σ-aryl anion released in Equation (6) and the added aryl halide (e.g., through an S_NAr process). Such reactions are known to be difficult and to require activated aryl halides. Yet, it must be emphasized that this statement is based upon the reported reactivity of anions in their usual form. The much higher energy of a *free* aryl anion Ar^- (i.e., not ion-paired and poorly solvated in THF) could possibly allow an aromatic nucleophilic substitution to take place [Eq. (12)].[15] If operating,

$$Ar-Pd^0L_2^- \underset{+Pd^0L_2}{\overset{-Pd^0L_2}{\rightleftharpoons}} Ar^- \xrightarrow{Ar'X'} Ar-Ar' + X'^- \qquad (12)$$

the sequence in Equation (12) would be kinetically equivalent to that in Equation (10) and would produce a similar kinetic artifact. To test for a possible kinetic interference of this type, aryl anions were generated electrochemically, by the direct two-electron reduction of an aryl halide,[16] in the presence of a second aryl halide, and their possible reaction was monitored. This procedure reproduces the above situation without the interference of palladium complexes. Figure 3 shows the result of such an experiment, in which 2-iodothiophene (ThI) is reduced in an overall two-electron[17] process, corresponding to wave R_2, to generate a σ-thienyl anion [Eq. (13–15)]. When the same

$$ThI + e^- \longrightarrow ThI^{\cdot -} \qquad (13)$$

$$ThI^{\cdot -} \longrightarrow Th^{\cdot} + I^- \qquad (14)$$

$$Th^{\cdot} + e^- \longrightarrow Th^- \qquad (15)$$

experiment is performed in the presence of iodobenzene (one equivalent) wave R_2 is not affected and is followed at more negative potentials by the unaffected two-electron[17] reduction wave R'_2 of iodobenzene. The voltammogram in Figure 3 (solid curve) is the exact superimposition of those of iodothiophene and iodobenzene recorded separately; this shows that there is no interaction between the two electrochemical processes. Furthermore, there is absolutely no evidence of any reduction process taking place at the potential where the reduction wave of Th–Ph, the biaryl product of a S_NAr reaction should be observed (see the vertical pointer in Fig. 3).[19] This is clear evidence that, despite their increased reactivities under our experimental conditions, the free σ-aryl anions produced in reaction (15) cannot undergo any reaction with aryl halides within the timescale investigated in this work.[20]

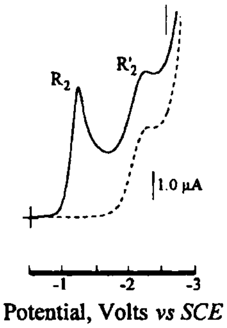
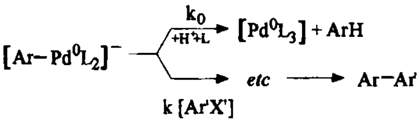


Fig. 3. Linear-sweep voltammetry of 2-iodothiophene, 2 mM in THF, 0.3 M NBu_4BF_4, in the presence of 2 mM PhI (solid curve). The voltammogram of 2 mM PhI alone under identical conditions is also shown (dashed curve) for comparison (see text). The vertical pointer at −2.60 V vs. SCE indicates the position where the reduction wave of 2-phenylthiophene (R_3) should be observed if this species were produced (see text). Gold disk electrode (diameter 0.5 mm), $v = 0.5\ Vs^{-1}$, 20 °C.

The two series of experiments described above establish that, in the presence of one equivalent of triphenylphosphine, any variation of the peak current of the oxidation wave O_2 as a function of increasing concentrations of aryl halide reflects only the direct reaction between $Ar-Pd^0L_2^-$ and the aryl halide (vide infra). Such a reaction necessarily occurs in concurrence with the spontaneous decomposition of the palladium intermediate (i.e., through the sequences in Eqs. (7) and (11), where E^+ is now a proton source).[7a] This is summarized in Scheme 2; the spontaneous decomposition of $Ar-Pd^0L_2^-$ (upper route) is de-



Scheme 2.

picted as an irreversible first-order reaction (with a single rate constant k_0) to stress that, in the presence of one equivalent of PPh_3, the sequence given by Eqs. (6 + 7) and (11) is irreversible and kinetically equivalent to a first-order reaction.[21] Under these conditions, the system at hand is kinetically equivalent to a competition between two first-order processes: one corresponding to the irreversible decomposition of $Ar-Pd^0L_2^-$ and the other to its reaction with the added aryl halides.

Quantitative Kinetic Investigation of the Reaction between $Ar-Pd^0L_2^-$ and Aryl Halides: The method used here involves the comparison of the peak currents of wave O_2 measured in the presence (designated i) or in the absence (designated i_0) of an aryl halide; both experiments were performed in the presence of one equivalent of triphenylphosphine. Indeed, the current magnitude of wave O_2 reflects quantitatively the amount of anionic arylpalladium(0) complex in the diffusion layer surviving over the time required to scan the potential from wave R_1, where it is created [Eq. (5)], to wave O_2, where it is detected. The present kinetic analysis is performed in THF to avoid the kinetic complications due to the CE sequence [Eq. (9)] that occurs in DMF, and, more importantly, because the background current in the potential range where wave O_2 is observed is more reproducible in THF than in DMF (cf. Figs. 2a and b). However, it was checked that all the results reported and discussed here for THF are qualitatively valid in DMF.

Based on Scheme 2, the variation of the average concentration of $Ar-Pd^0L_2^-$ due to chemical reactions taking place in the diffusion layer during the voltammetric scan obeys the rate law given in Equation (16) (see Experimental Section),[22] where k_0

$$\{d[Ar-Pd^0L_2^-]_{av}/dt\}_{chem} = -(k_0 + k[Ar'X'])[Ar-Pd^0L_2^-]_{av} \qquad (16)$$

is the intrinsic overall rate constant describing the spontaneous first-order decay of $Ar-Pd^0L_2^-$ in the absence of added aryl halide,[21] and k is the rate constant of the reaction between $Ar-Pd^0L_2^-$ and the added aryl halide Ar'X' (see Scheme 2). It follows from Equation (16) that the peak current of the oxidation wave O_2 is given by Equation (17) (see Experimental Section), where, for a given $Ar-Pd^0L_2^-$ complex, $\mathscr{A}$ is constant for constant values of the scan rate (v) and of $\Delta E = (E^p(O_2) + E^p(R_1) - 2E_{inv})$; E_{inv} is the value at which the direction of the potential scan is inverted after wave R_1 is scanned. When an *identical* voltammetric scan (i.e., same E_{inv}, same scan rate) is performed in the absence of added aryl halide, the same equation applies with [Ar'X'] = 0 [Eq. (18)]. From Equations (17) and (18), Equation (19) is readily deduced.

$$i \approx \mathscr{A} \exp\{-(k_0 + k[Ar'X'])(\Delta E/v)\} \qquad (17)$$

$$i_0 \approx \mathscr{A} \exp\{-k_0(\Delta E/v)\} \qquad (18)$$

$$\ln(i_0/i) \approx k[Ar'X'](\Delta E/v) \qquad (19)$$

Equation (19) is tantamount to a first-order homogeneous kinetic plot since $\Delta E/v$ is the duration of the electrochemical kinetic experiment.[12] On the one hand, it provides a verification of the order of the reactions of $Ar-Pd^0L_2^-$ and Ar'X' (cf. e.g. Fig. 4a),[22] and, on the other hand, it allows the values of the bimolecular rate constants k to be determined for different combinations of $Ar-Pd^{II}XL_2$ and Ar'X' [Eq. (20)].

$$p\text{-}Z\text{-}C_6H_4\text{-}Pd^0(PPh_3)_2^- + p\text{-}Z'\text{-}C_6H_4I \xrightarrow{k_{ZZ'}} \text{etc.} \qquad (20)$$

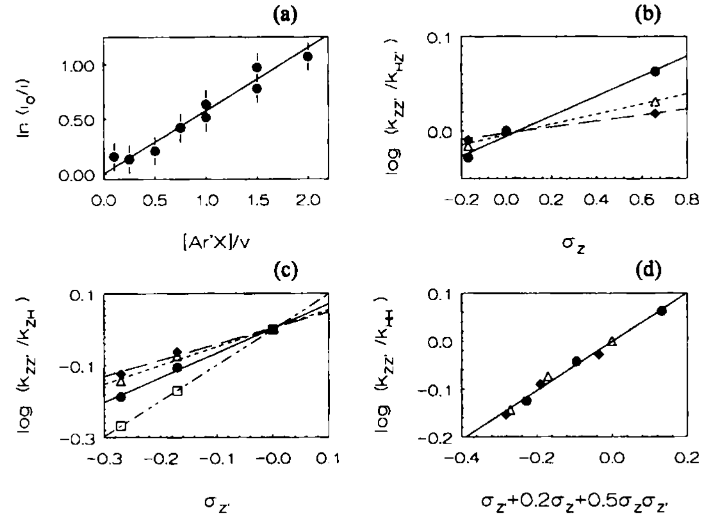


Fig. 4. Reactivity of phenyl iodides with arylpalladium(0) anionic complexes (see text and Eqs. (19-22)). a) Kinetic plot (see Eq. (19)) for the reaction of *p*-iodotoluene (Ar'X') with 2-thienyl-$Pd^0(PPh_3)_2^-$, 2 mM, in the presence of PPh_3, 2 mM. i_0 and i: peak currents of wave O_2 in the absence and in the presence of Ar'X', respectively (see text and compare Figs. 1a and 1c; [Ar'X'] in equivalents (1 to 5); v in 100 Vs^{-1} units). b-d) Hammett correlations for reactions of substituted phenylpalladium(0) anionic complexes (p-Z-$C_6H_4-Pd^0L_2^-$ or 2-$C_4H_3S-Pd^0L_2^-$) with substituted phenyl iodides (p-Z'-C_6H_4-I) in the presence of 1 equiv of PPh_3 (see Eq. (20) and text): b) Z' = Me (▲), H (●), or MeO (◆). c) Z = CN (●), H (▲), or Me (◆); 2-thienyl-$Pd^0(PPh_3)_2^-$ (□). d) Generalized Hammett correlation; Z = CN (●), H (▲), or Me (◆). Conditions: THF, 0.3 M NBu_4BF_4, gold disk electrodes (diameters 0.5 or 0.1 mm), 20 °C.

Table 3. Rate constants k (in $10^4\,M^{-1}s^{-1}$) [a] of reaction (20) between anionic zerovalent palladium complexes ($Ar-Pd^0(PPh_3)_2^-$) and *para*-substituted phenyl iodides p-Z'-C_6H_4-I in THF, 0.3 M NBu_4BF_4, 20 °C.

		Z' = MeO	Z' = Me	Z' = H
p-Z-$C_6H_4-Pd^0L_2^-$	Z = Me	1.5	1.8	2.3
	Z = H	1.4	1.7	2.0
	Z = CN	1.4	1.6	1.9
2-$C_4H_3S-Pd^0L_2^-$		1.1	1.4	2.1

[a] Rate constants were determined according to Equation (19), with ΔE values determined from peak potentials reported in Table 2 [33].

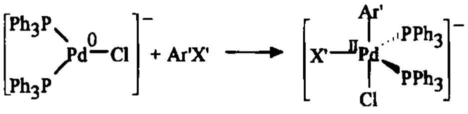
The rate constants for reaction (20) are reported in Table 3. It is noteworthy that all these rates fall within the same range ($1-2.5 \times 10^4\,M^{-1}s^{-1}$); this shows that the reaction between $Ar-Pd^0L_2^-$ and aryl halides is quite insensitive to electronic factors. Precise Hammett correlations can, however, be performed by using i_0/i values determined at an identical scan rate and for constant ΔE values.[23] Indeed, the ratio of Equations (19) for two different aryl halide/palladium systems gives Equation (21),

$$k_{ZZ'}/k_{HH} = \{\log(i_0/i)_{v,ZZ'}/\log(i_0/i)_{v,HH}\}\{[C_6H_5I]/[p\text{-}Z'\text{-}C_6H_4I]\} \qquad (21)$$

which yields a higher precision than would be obtained with the data in Table 3, since all uncertainties regarding the duration of the experiment (i.e., related to $\Delta E/v$, see Experimental Section) cancel. Figures 4b,c show the corresponding individual Hammett correlations as a function of the substituent borne either by the phenyl ligand of the zerovalent palladium moiety ($Ar-Pd^0L_2^-$ = p-Z-$C_6H_4-Pd^0L_2^-$; Z' = constant; Fig. 4b) or by the phenyl iodide (Ar'I = p-Z'-C_6H_4I; Z = constant; Fig. 4c). The presence of electron-withdrawing groups on either phenyl moiety contribute to enhance the rate of oxidative addition, and, as expected, the larger effects (i.e., the larger ρ values) arise from the substituents Z′ borne by the aryl halide (p-Z′-C_6H_4I). Less expected is the fact that the rate of oxidative addition increases with increasing electron-withdrawing effect of the substituent Z borne by the aryl ligand of the palladium center (the effect is much smaller than that of Z′, by a factor of about one fifth). Moreover, the electronic effects of each substituent are synergistic, as evidenced by the requirement of a coupling term (namely, $\sigma_Z\sigma_{Z'}$) in the generalized Hammett equation [Eq. (22)] (correlation coefficient 0.993; 9 data points; Fig. 4d).

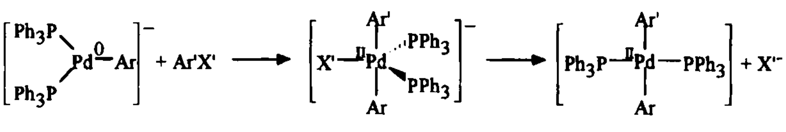
$$\log(k_{ZZ'}/k_{HH}) = 0.51\,(\sigma_{Z'} + 0.2\,\sigma_Z + 0.5\,\sigma_Z\sigma_{Z'}) \qquad (22)$$

This establishes that both aryl groups participate in the stabilization of the transition state of the oxidative addition of Ar′X′ with Ar-$Pd^0L_2^-$, yet not totally symmetrically. If the transition state were a late one, one would expect a better symmetry between the two aryl groups. On the other hand, if the transition state were an early one, one would expect electron-withdrawing substituents of the aryl group borne by the palladium center to have a negative effect on the reaction rate. Indeed, the electron density at the palladium center of p-Z-C_6H_4-$Pd^0L_2^-$ is anticipated to decrease with increasing electron-withdrawing ability of Z; this would result in a decrease in reaction rate (negative ρ). Thus, the small but positive value (0.1) of the σ_Z coefficient in Equation (22), as well as the positive coupling term ($0.25\sigma_Z\sigma_{Z'}$) suggests that the transition state is located nearly half-way along the reaction coordinate. Finally, it may be worth emphasizing that the poor selectivity of reactions (20) compared to the analogous reactions shown in Scheme 3,[8,24a] in which the zerovalent palladium center is ligated by a halide, is associated with the difference in the reaction rates: the former are approximatively forty times faster than the latter.[8a]



Scheme 3.

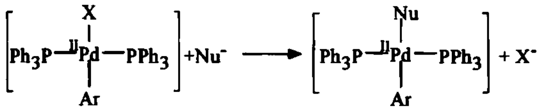
By analogy with Scheme 3, it can be postulated that Equation (20) also gives a pentacoordinated anionic species, in which the Cl of Scheme 3 is replaced with an aryl ligand (Scheme 4). If formed, such an intermediate would be expected to dissociate to give a *trans*-bisarylpalladium(II) complex, which seems to be necessary to account for the fact that the reaction eventually yields a biaryl product (Table 1, entries 1,2).[1-2,9,25] On the other hand, if there is no intermediate, the *trans*-bisarylpalladium(II) should be formed directly together with one mole of halide ion. At low scan rates (e.g., in Fig. 1c), one observes i) an oxidation wave O_4 for iodide ions ($E^p = 0.40$ V vs. SCE at 0.2 Vs^{-1}), which is evidence that these ions have been released in the medium, and ii) a substantial deficit of oxidizable palladium centers, as is, for example, shown by the fact that the sum of the oxidation currents of waves O_2 and O_3 in Figure 1c is much less than in Figure 1a.[10b] Both these facts are compatible with the formation of a non-oxidizable palladium center and an iodide ion within the timescale of the experiment shown in Figure 1c, that is, they are in agreement with the overall reaction shown in Scheme 4.



Scheme 4.

However, when the timescale is decreased to a few tens of milliseconds (Fig. 1d), wave O_4 is not yet present (cf. the vertical marker in Fig. 1d), while a broad oxidation current is observed between waves O_2 and O_3, that is, in the range between approximately 0 and 0.2 V vs. SCE. The absence of wave O_4, corresponding to the free iodide ions,[10b] indicates that they have not yet been released into the diffusion layer, although the reaction of Ar-$Pd^0L_2^-$ with the added aryl halide has already proceeded to a significant extent ($t_{1/2} \approx 7$ ms under the conditions of Fig. 1d, cf. Table 3). This establishes that the reaction in Scheme 4 proceeds through a transient intermediate that contains an iodide ligand. Moreover, owing to the potential shift (ca. 400 mV more negative) observed between the oxidation of Cl-$Pd^0(PPh_3)_2^-$ [24] and that of Ph-$Pd^0(PPh_3)_2^-$,[7a] and based on the oxidation waves at around 0.40 V vs. SCE determined for the oxidation of the chloride-ligated pentacoordinate anionic species formed in Scheme 3,[24] one would expect to observe an oxidation wave at around 0–0.1 V vs. SCE for the analogous anionic pentacoordinated intermediate postulated in Scheme 4, that is, precisely in the potential range where a broad current wave is observed (Fig. 1d). Although this evidence cannot be regarded as a proof for the existence of such an intermediate, together with the above-mentioned deficit of iodide ions, it strongly suggests that Scheme 4 proceeds via a pentacoordinate intermediate similar to that previously observed for the halide analogue (Scheme 3).[24] However, owing to the fact that this reaction intermediate in Scheme 4 forms and dissociates on approximatively the same timescale, a better characterization is impossible.

Mechanism of Palladium-Catalyzed Homocoupling of Aryl Halides: The final species formed in Scheme 4 has been postulated above to be a palladium(II) bisaryl species by analogy with the classical *trans*-palladium(II) intermediates generated upon nucleophilic substitution of *trans*-Ar-$Pd^{II}XL_2$ in palladium-catalyzed nucleophilic substitutions (Scheme 5).[1,3,25a] Indeed, since the latter are prone to undergo reductive elimination of the Ar-Nu moiety,[1,3,25a] it is probable that the non-oxidizable palladium species yielding the bisaryl products identified in Table 1 is a bisarylpalladium(II) complex. Reductive elimination of Ar-Ar′ from such an intermediate would regenerate a low-coordinate zerovalent palladium complex.[25c] Based on our previous results,[8a] we expect that the latter species rapidly coordinates a halide ion to afford X-$Pd^0L_2^-$ to which a new aryl halide molecule readily adds oxidatively (Scheme 3).[8a,24] This generates a pentacoordinated halide-ligated arylpalladium(II) species, which is then readily reduced at a potential close to that of wave R_1 to regenerate the Ar-$Pd^0L_2^-$ anion.[24] This last step closes the catalytic cycle presented in Scheme 6. Note that in Scheme 6, the steps that have been characterized in this study or in previous ones[7a,8a] are



Scheme 5.

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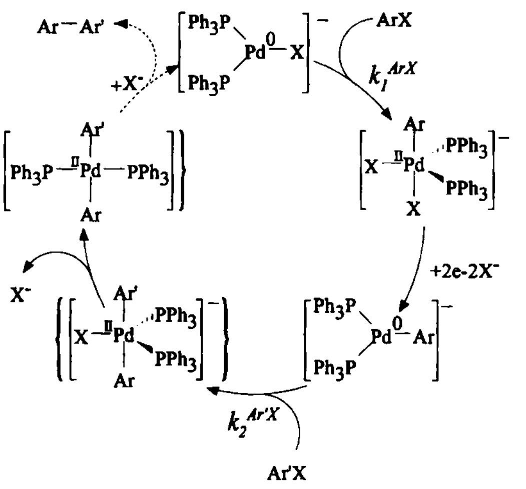

Scheme 6.

indicated by solid arrows, whereas the step postulated on the basis of established chemistry is represented by a dashed arrow. Similarly, the two intermediates that are postulated on the basis of kinetics but that could not be fully characterized in this study are enclosed between braces; all other intermediates have been characterized here or previously.

The mechanism in Scheme 6 is quite different from that reported previously[16a, b] for the same overall process catalyzed by nickel(dppe). In the nickel catalytic cycle, one aryl halide reacts with a Ni^0 center whereas the second one reacts with a $Ar-Ni^I$ species, a situation which is impossible here because of the overall bielectronic reduction of the palladium(II) species considered here. Indeed, in Scheme 6, two aryl halides are activated sequentially by two different anionic zerovalent palladium species: one aryl halide oxidatively adds to the halide-ligated bisphosphine palladium(0) center,[8a, 24] whereas the other adds to the aryl-ligated analogue formed upon two-electron reduction of the anionic pentacoordinate palladium(II) species resulting from the first oxidative addition. Both steps have been established and characterized kinetically in this or previous studies.[8a, 24]

Since the activation of each aryl halide occurs at different palladium(0) centers, we can evaluate the chances of catalyzing heterocoupling reactions through the sequence in Scheme 6. The first oxidative addition (i.e. to $X-Pd^0L_2^-$; rate constant k_1^{ArX} in Scheme 6) is expected to be rather selective, based on its significant dependence on the electronic properties of the aryl halide ($\rho_1 = 2$ to 2.7 depending on the nature of the halide ion and its concentration).[8a] In contrast, the second oxidative addition (i.e. to $Ar-Pd^0L_2^-$; rate constant $k_2^{Ar'X}$ in Scheme 6) is hardly affected by the electronic properties of the aryl halide since $\rho_2 \approx 0.5$ [Eq. (22)]. The catalytic sequence in Scheme 6 is therefore expected to afford a nearly statistical product distribution (i.e., $^1/_4$Ar–Ar, $^1/_2$Ar–Ar', $^1/_4$Ar'–Ar') when the two aryl halides are present at identical initial concentrations.

To check the validity of the above conclusion, a series of preparative electrolyses was performed in THF and in DMF. In THF, despite the fact that the reaction proceeds readily within the voltammetric timescale, no significant yields of homo- or heterobiaryls could be obtained on the preparative scale. We observed mainly degradation products resulting from coupling of aryl moieties originating from the aryl halide(s) and those borne by the phosphine ligand of the palladium species.[27] We ascribe this behavior to a degradation of the bisarylpalladium(II) species under our reductive (and therefore basic) conditions in THF during the long electrolysis time.[28] However, we know from results previously reported by some of us that the palladium-catalyzed homocoupling of aryl halides proceeds smoothly in DMF (Table 1, first two rows).[9] Based on our above voltammetric investigation, the kinetic behavior in the two solvents is qualitatively identical during the short timescale of cyclic voltammetry. Therefore our kinetic conclusions based on our study in THF are expected to be transposable to DMF. We therefore attempted to catalyze heterocoupling reactions by the same procedure in DMF. The result shown in Table 1, third row, establishes that, in agreement with our above conclusion based on Scheme 6, a nearly statistical distribution of biaryls is obtained when two aryl halides in a 1:1 ratio react in the presence of catalytic amounts of palladium complex.

Based on Scheme 6 it is, however, predicted that, when the reaction is performed in a two-step batch procedure with stoichiometric amounts of palladium complex, good yields of heterocoupled products should be obtained. In a first step, $Pd^{II}Cl_2(PPh_3)_2$ is reduced (2 F mol^{-1}) to the zerovalent reactive anion $Cl-Pd^0(PPh_3)_2^-$, and one equivalent of the first aryl iodide (ArI) reacts quantitatively with the electrolyzed solution to afford the corresponding anionic pentacoordinated arylpalladium species $Ar-Pd^{II}ICl(PPh_3)_2^-$.[24] In a second step, this species is reduced (2 F mol^{-1})[24, 26] in the presence of one equivalent of the second aryl iodide Ar'I, and the sequence indicated in Scheme 6 is repeated. This occurs in the absence of the first aryl halide, which has already been consumed during the first step. Formation of homocoupling products is thus largely prevented. In agreement with this prediction based on Scheme 6, the procedure outlined above was found to give a much improved yield (76%) of the heterocoupled product Ar–Ar'.

Conclusion

The reactivity of tris-ligated anionic zerovalent complexes, $Ar-Pd^0L_2^-$, with a series of *para*-substituted phenyl iodides has been investigated kinetically. It was shown that the reaction is almost insensitive to electronic properties of the aryl halide, in contrast to what we reported previously for the analogous halide-ligated species $X-Pd^0L_2^-$. Several experimental pieces of evidence suggest that the product of the reaction is a halide-ligated pentacoordinate anionic bisarylpalladium(II) intermediate, which rapidly decays within a few milliseconds to afford, presumably, a classical *trans*-bisarylpalladium(II) species known to readily eliminate a biaryl. Because of the very short lifetime of this intermediate, it was impossible to establish this conclusively.

Based on this mechanism and on our previous results, a catalytic cycle has been proposed to account for the palladium catalyzed homocoupling of aryl halides (Scheme 6). This cycle is initiated by oxidative addition of a first molecule of aryl halide to a zerovalent low-coordinate palladium center. Two-electron reduction of the anionic pentacoordinated arylpalladium(II) species thus formed leads to an anionic arylpalladium(0) center, which undergoes oxidative addition by a second aryl halide molecule within a millisecond timescale. This affords a transient palladium(II) species which is tentatively described here as a pentacoordinate anionic bisarylpalladium(II) complex. This species undergoes fast decomposition by expulsion of its halide ligand within a timescale of a few milliseconds, most probably to afford a neutral bisarylpalladium(II) complex. Reductive elimination of a biaryl molecule from this center is then thought to close the catalytic cycle, by restoring the initial zerovalent palladium complex. Although all the steps of this chain have been characterized kinetically, except for the reductive elimination step, the exact nature of the pentacoordinate anionic bisarylpalladium(II) complex (and hence that of its decay product, the neutral bisarylpalladium(II) complex) could only be inferred from kinetic results, owing to its very short lifetime ($t_{1/2} \approx 1$ ms) which is comparable to its rate of production.

Based on these mechanistic results and Hammett correlations relative to the two oxidative steps that control the selectivity in Scheme 6, it was concluded and verified experimentally in DMF that only batch procedures, with stoichiometric amounts of a palladium complex, could lead to high yields in heterocoupling products.

Experimental Section

Chemicals: Aromatic halides were obtained from commercial sources, and $Pd^0(PPh_3)_4$ was prepared according to a reported procedure [29]. *trans*-Ar–$Pd^{II}X(PPh_3)_2$ complexes were synthesized according to published procedures [30]. For Ar = *p*-substituted phenyls, the spectra (^1H NMR) of the products were identical to those reported previously [7a]. Complexes with Ar = 2-thienyl have not been reported previously. They were characterized as follows. $2\text{-}C_4H_3S\text{-}Pd^{II}Br(PPh_3)_2$: m.p. 155 °C; ^1H NMR (250 MHz, $CDCl_3$, vs. TMS): δ = 6.02 (d, J = 3.7 Hz, 1 H), 6.44 (dd, J = 5 Hz, J = 3.7 Hz, 1 H), 6.94 (d, J = 5 Hz, 1 H), 7.39 (m, 18 H), 7.63 (m, 12 H). $2\text{-}C_4H_3S\text{-}Pd^{II}I(PPh_3)_2$: m.p. 145 °C; ^1H NMR (250 MHz, $CDCl_3$, vs. TMS): δ = 5.90 (d, J = 3.7 Hz, 1 H), 6.35 (dd, J = 5 Hz, J = 3.7 Hz, 1 H), 6.82 (d, J = 5 Hz, 1 H), 7.30 (m, 18 H), 7.54 (m, 12 H). The cross-coupling product $2\text{-}(C_4H_3S)\text{-}C_6H_5$ was synthesized according to the procedure given in ref. [3e] by treating 2-thienyl-MgBr with PhI in the presence of catalytic amounts of $Pd^0(PPh_3)_4$. Yield: 83 %. White crystals, m.p. 38 °C. ^1H NMR (250 MHz, $CDCl_3$, vs. TMS): δ = 7.10 (dd, J = 5 Hz, J = 3.7 Hz, 1 H), 7.31 (m, 3 H), 7.40 (t, J = 7.3 Hz, 2 H), 7.63 (d, J = 7.7 Hz, 2 H).

Instrumentation and Procedures: Cyclic voltammetry experiments were performed with the same setup and apparatus described in previous papers published by some of us [6,7a,24]. Absolute electron number consumption in cyclic voltammetry were determined according to the procedure described in ref. [31]. The electrolysis experiments reported in Table 1, including those in the two first rows which are taken from ref. [9], were carried out in an H-shaped divided cell fitted with lead cathode (1.5×2 cm²) and platinum anode (1.5×2 cm²) under galvanostatic conditions. The constant electrolysis current was supplied by a constant dc current power supply. Charge consumptions were determined by measuring the duration of electrolysis (i.e. $Q = it$).

IR spectra were obtained on a JEOL RFX-3002 grating infrared spectrophotometer. ^1H NMR spectra performed in Okayama (for Table 1) were recorded with a Varian VXR-200 MHz spectrometer. ^1H NMR spectra performed in Paris (for the complexes considered in Table 2) were recorded with a Bruker AC-250 MHz spectrometer. In both cases, chemical shifts are reported in part per million (δ) relative to tetramethylsilane (δ = 0.00) as an internal standard in $CDCl_3$ solution. Melting points were determined with a Buchi 510 apparatus.

Typical Procedures for Electrolysis:

Electroreductive Coupling of 4-tert-Butylphenyl Iodide (1) [9]: A mixture of **1** (78 mg, 0.3 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), and PPh_3 (11 mg, 0.04 mmol) in DMF (5 mL) containing Et_4NOTs (0.5 g) was charged into the cathode compartment. The anode compartment was filled with a DMF solution (5 mL) of Et_4NOTs (0.5 g). The electrolysis cell was purged with argon gas, and a regulated dc current (2.5 mA cm⁻²) was passed at room temperature. After the passage of 3.7 F mol⁻¹ of electricity (4 h), most of the starting material **1** was consumed. The catholyte was poured into brine and extracted with toluene/ether (1/1). The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed on SiO_2 with hexane/EtOAc (10/1) to afford 4,4'-di-*tert*-butylbiphenyl (**3**) (39 mg, 97 %): ^1H NMR (200 MHz, $CDCl_3$, vs. TMS): 1.36 (s, 18 H), 7.44 (d, J = 8.6 Hz, 4 H), 7.52 (d, J = 8.6 Hz, 4 H); IR (KBr): $\tilde{\nu}$ = 3030, 2960, 1497, 1365, 1267, 1116, 1033, 822 cm⁻¹.

Electroreductive Coupling of 4-(N,N-Dimethylamino)phenyl Iodide (2) [9]: A mixture of **2** (74 mg, 0.3 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), and PPh_3 (11 mg, 0.04 mmol) in DMF (5 mL) containing Et_4NOTs (0.5 g) was electrolyzed in a similar manner to that described above. After passage of 4.7 F mol⁻¹ of electricity (2.5 mA cm⁻², 5 h), the catholyte was poured into brine and extracted with toluene/ether (1/1). The extracts were washed with brine, dried (Na_2SO_4), concentrated in vacuo, and chromatographed on SiO_2 with hexane/EtOAc (5/1) to afford 4,4'-bis(*N*,*N*-dimethylamino)biphenyl (**5**) (33 mg, 92 %): ^1H NMR (200 MHz, $CDCl_3$, vs. TMS): δ = 2.89 (s, 12 H), 6.68 (d, J = 8.7 Hz, 4 H), 7.06 (d, J = 8.7 Hz, 4 H); IR (KBr): $\tilde{\nu}$ = 3000, 1610, 1520, 1440, 1340, 1232, 1160, 1070, 946, 830, 790 cm⁻¹.

Electroreductive Heterocoupling of 4-tert-Butylphenyl Iodide (1) and 4-(N,N-Dimethylamino)phenyl Iodide (2): **Procedure A:** A mixture of **1** (78 mg, 0.3 mmol), **2** (74 mg, 0.3 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), and PPh_3 (11 mg, 0.04 mmol) in DMF (5 mL) containing Et_4NOTs (0.5 g) was charged into the cathode compartment and electrolyzed in a similar manner to that described above. After passage of 95 C (2.5 mA cm⁻², 3.5 h), workup of the catholyte afforded 4,4'-di-*tert*-butylbiphenyl (**3**) (17 mg, 21 %), 4-*tert*-butyl-4'-(*N*,*N*-dimethylamino)biphenyl (**4**) (34 mg, 45 %), and 4,4'-bis-*N*,*N*-dimethylamino)biphenyl (**5**) (17 mg, 24 %). ^1H NMR spectra and IR spectra of **3** and **5** were identical with those described above. **4**: ^1H NMR (200 MHz, $CDCl_3$, vs. TMS): 1.56 (s, 9 H), 2.90 (s, 6 H), 6.50 (d, J = 9.1 Hz, 2 H), 7.15 (d, J = 8.6 Hz, 2 H), 7.48 (d, J = 9.1 Hz, 2 H), 7.62 (d, J = 8.6 Hz, 2 H); IR (neat): $\tilde{\nu}$ = 3080, 1593, 1493, 1394, 1365, 1110, 1004, 820, 717 cm⁻¹.

Procedure B: A mixture of $PdCl_2(PPh_3)_2$ (211 mg, 0.3 mmol) and PPh_3 (157 mg, 0.6 mmol) in DMF (5 mL) containing Et_4NOTs (0.5 g) was placed in the cathode compartment, and regulated dc current (2.5 mA cm⁻²) was supplied. After passage of 2.2 F mol⁻¹ based on $PdCl_2(PPh_3)_2$ (2.4 h), the dc current was interrupted, and **2** (74 mg, 0.3 mmol) was added to the cathode compartment. The mixture was then stirred at room temperature for 0.5 h. Iodide **1** (78 mg, 0.3 mmol) was then added, and the regulated dc current (2.5 mA cm⁻²) was passed again through the mixture. After passage of additional 3.5 F mol⁻¹, the catholyte was poured into brine and extracted with toluene/ether (1/1). The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Column chromatography of the residue on SiO_2 with hexane/EtOAc (10/1) afforded **4** (58 mg, 76 %) together with **3** (6 mg, 8 %) and **5** (8 mg, 11 %). ^1H NMR spectra and IR spectra of **3**, **4**, and **5** were identical in all respects to those described above.

Derivation of the Rate Law in Equations (16–19): At a planar electrode, under planar and semi-infinite diffusion conditions, the concentration of the arylpalladium(0) anion in the diffusion layer is given by the partial derivative Equation (23) [12,22], where x is the distance from the electrode surface and D the diffusion coefficient.

$$\begin{aligned}&\partial[\mathrm{Ar{-}Pd^0L_2^-}]/\partial t = \\ &\mathrm{D}\,\partial^2[\mathrm{Ar{-}Pd^0L_2^-}]/\partial x^2 - (k_0 + k[\mathrm{Ar'X'}])[\mathrm{Ar{-}Pd^0L_2^-}]\end{aligned} \tag{23}$$

Integrating both sides of the above equation over δ [32], which is the maximum value of the diffusion layer thickness, we obtain Equation (24) ([Ar'X'], being

$$\begin{aligned}\partial\{\textstyle\int_0^\delta[\mathrm{Ar{-}Pd^0L_2^-}]\mathrm{d}x\}/\partial t = &- \mathrm{D}\{\partial[\mathrm{Ar{-}Pd^0L_2^-}]/\partial x\}_{x=0} \\ &- (k_0 + k[\mathrm{Ar'X'}])\{\textstyle\int_0^\delta[\mathrm{Ar{-}Pd^0L_2^-}]\mathrm{d}x\}\end{aligned} \tag{24}$$

in excess, is assumed to be constant). Since $\mathrm{Ar{-}Pd^0L_2^-}$ is not electroactive over the potential range spanned during the backward voltammetric scan between waves R_1 and O_2, its gradient at the electrode surface is zero; thus, Equation (25) can be

$$\begin{aligned}&\partial\{\textstyle\int_0^\delta[\mathrm{Ar{-}Pd^0L_2^-}]\mathrm{d}x\}/\partial t = \\ &- (k_0 + k[\mathrm{Ar'X'}])\{\textstyle\int_0^\delta[\mathrm{Ar{-}Pd^0L_2^-}]\mathrm{d}x\}\end{aligned} \tag{25}$$

derived. Introducing the average concentration of $\mathrm{Ar{-}Pd^0L_2^-}$ within the diffusion layer [Eq. (26)] allows the above differential equation to be rewritten [32] in the form

$$[\mathrm{Ar{-}Pd^0L_2^-}]_{\mathrm{av}} = \{\textstyle\int_0^\delta[\mathrm{Ar{-}Pd^0L_2^-}]\mathrm{d}x\}/\delta \tag{26}$$

of Equation (16) given in the text [Eq. (27)], where the mathematically correct partial derivative formulation (i.e. the '∂ /∂t' operator) is replaced by the symbolism

$$\begin{aligned}\partial[\mathrm{Ar{-}Pd^0L_2^-}]_{\mathrm{av}}/\partial t &= -(k_0 + k[\mathrm{Ar'X'}])[\mathrm{Ar{-}Pd^0L_2^-}]_{\mathrm{av}} \\ &= \{\mathrm{d}[\mathrm{Ar{-}Pd^0L_2^-}]_{\mathrm{av}}/\mathrm{d}t\}_{\mathrm{chem}}\end{aligned} \tag{27}$$

"$\{\mathrm{d}/\mathrm{d}t\}_{\mathrm{chem}}$" to indicate that only chemical kinetics need to be considered, since the effect of diffusion is already taken into account by the previous integration. Straightforward integration of Equation (27), over the time $\Delta t = (\beta\Delta E/v)$ [32,33] required to span the potential from wave R_1 to wave O_2, affords Equation (28),

$$[\mathrm{Ar{-}Pd^0L_2^-}]_{\mathrm{av}}/C^0 = \mathcal{A}(\beta\Delta E/v)\exp\{-(k_0 + k[\mathrm{Ar'X'}])(\beta\Delta E/v)\} \tag{28}$$

where $\mathcal{A}(\beta\Delta E/v)$ is a function of the parameter $\beta\Delta E/v$ only and is introduced to account for the spatial extension of the concentration profile during the time $\beta\Delta E/v$ because of diffusion [32,33]. Because of the presence of the parameter β [32,33], Equations (17–19) are not mathematically rigorous. However, the relative systematic errors in the rate constant ratios arising from the use of these approximate rate laws are considerably less than the experimental errors introduced by the determinations of i_0/i. Indeed, $\beta = 1$ as in Equations (17–19) introduces a systematic relative error of only 3 % in the rate constants measurement, since $\beta = 0.97$ [33]. Since the value of the function $\mathcal{A}$ depends only on the voltammetric scan (ΔE and v) and on the wave shapes (β) [33], it is independent of the presence or of the absence of Ar'X'. Thus, although the individual currents depend on the function $\mathcal{A}$, the ratio i_0/i, used in Equation (19) is independent of $\mathcal{A}$. For this reason the evaluation of $\mathcal{A}$ is not required in this study. Similarly, provided that only experiments with identical scans (i.e. same ΔE and v) and waves with comparable half-widths (i.e. same β) are compared, the factors $\mathcal{A}$ and ($\beta\Delta E/v$) cancel in Equation (21), giving rise to a better precision in the relative rate constants than in individual measurements (Table 3).

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[2] For reviews, see: a) R. F. Heck, *Acc. Chem. Res.* **1979**, 12, 146. b) M. Kumada, *Pure Appl. Chem.* **1980**, *52*, 669. c) E. I. Negishi, *Acc. Chem. Res.* **1982**, *15*, 340. d) R. F. Heck, *Organic Reactions (NY)* **1982**, *27*, 345. e) R. F. Heck, *Palladium in Organic Synthesis*; Academic Press, New York, **1985**. f) J. K. Stille, *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

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[6] For a review and discussion of several electrochemical processes based on Eq. (4), see: a) C. Amatore, A. Jutand, *Organometallics* **1988**, 7, 2203. b) C. Amatore, A. Jutand, *Acta Chem. Scand.* **1990**, *44*, 755.

[7] a) C. Amatore, A. Jutand, F. Khalil, M. F. Nielsen, *J. Am. Chem. Soc.* **1992**, *114*, 7076. b) In (a), where Ar is a *para*-substituted phenyl ligand, two distinct oxidation peaks were observed for Ar–Pd^{0}L$_2^-$ (O$_2$) and Pd^{0}L$_2$ (O$_3$), but no peak (O*) could be observed for the phenyl anions (compare wave O* in Figs. 1 a–c when Ar is a 2-thienyl ligand), owing to the fast follow-up reactions of this species [Eq. (7)]. The observation of distinct peaks for Ar–Pd^{0}L$_2^-$ and Pd^{0}L$_2$ may appear kinetically incompatible with the existence of an equilibrium [Eq. (6)] between these species, since a fast equilibrium is expected to lead to the observation of a single oxidation peak (featuring a CE mechanism) [8] in the potential range where the first oxidation wave (i.e., O$_2$) is detected. This would be true in the absence of reaction (7), which consumes the aryl anion within the time required to span the potential between the peak of wave R$_1$ and the potential range where waves O$_2$, O$_3$, and possibly O* are found (compare the small size of this wave in Fig. 1 a). Thus, even when the equilibrium in Equation (6) is totally established at all scan rates considered, one expects to observe a wave O$_2$ corresponding to the concentration of Ar–Pd^{0}L$_2^-$ with a minor CE contribution due to the small amount of surviving aryl anions, followed by a wave O$_3$ corresponding to the reoxidation of Pd^{0}L$_2$, which cannot afford Ar–Pd^{0}L$_2^-$ [by the reverse reaction in Eq. (6)], because of partial or complete consumption of Ar$^-$. So under such circumstances (Ar = phenyl) a CE mechanism cannot take place at the electrode surface despite the reversibility of reaction (6) [7 a]. c) In the case of Figure 1, despite the greater stability of the 2-thienyl anion, the situation is very similar as evidenced by the small magnitude of the wave O*. Yet, the fact that this wave is present shows that the backward reaction of Equation (6) is much slower than in the case of the phenyl ligands, because otherwise this wave should be absent, all thienyl anions being consumed at the level of wave O$_2$ in a CE mechanism [12].

[8] a) C. Amatore, M. Azzabi, A. Jutand, *J. Am. Chem. Soc.* **1991**, *113*, 8375. b) For the general electrochemical behavior of CE mechanisms, see: A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, Wiley, New York. **1980**. pp. 443–451. c) Note that reaction of Pd^{0}L$_3$ with aryl halides is still possible [8 a], yet it requires timescales that are much longer than those considered here ($t \leq 100$ ms), because it must proceed via a transient Pd^{0}L$_2$ intermediate formed by the energetically unfavorable dissociation of Pd^{0}L$_3$ [reverse of Eq. (11)] [14]. d) Note that, in agreement with our previous observations [8 a], the oxidation of Pd^0(PPh$_3$)$_3$ formed in Equation (11) is observed in the same potential range where the oxidation of Pd^0(PPh$_3$)$_2$ occurs (wave O$_3$). The reason for the almost equal oxidation potentials is not yet clear. However, this does not in any way affect the oxidative process at wave O$_2$ (which occurs at less positive potentials) or the homogeneous steps. For this reason, and for sake of simplicity in the following, we use the same label for the two waves.

[9] S. Torii, H. Tanaka, K. Morisaki, *Tetrahedron Lett.* **1985**, 1655.

[10] a) In addition to wave O$_2$, which is the main wave at high scan rates, two other oxidation waves are also observed. One of these (labeled O$_3$) corresponds to the two-electron oxidation of the zerovalent palladium moiety formed in Equation (6) [7 a,b]. The second, labeled O* (cf. Fig. 1 a and Table 2), is observed only when the decomposition in Equation (6) affords σ-aryl anions with rather long lifetimes (i.e., larger than a few milliseconds, as for the 2-thienyl σ-anion *in this study*, but not for the substituted phenyl ones) and corresponds to the oxidation of the σ-aryl anion. b) In the presence of added aryl halide, ArI, a fourth oxidation wave, O$_4$, is also observed, corresponding to the oxidation of iodide ions (peak potential at 0.40 V vs. SCE for 0.2 Vs^{-1}). In the absence of added aryl halide, wave O$_4$ is not observed because iodide ions are quantitatively consumed during the oxidations of palladium(0)-based complexes (2 equiv of halide ligands are formally required per palladium center oxidized in order to generate a stable Pd^{II}XYL$_2$ species at waves O$_2$ and O$_3$) and are therefore scavenged from the electrode vicinity (for a discussion of this effect see ref. [24]). This is no longer true when an excess of iodide ions is present in the diffusion layer, with respect to the overall amount of oxidizable palladium species. In other words, the observation of wave O$_4$ under our present experimental conditions is a proof that a significant fraction of palladium species generated at wave R$_1$ is present in the diffusion layer in a non-oxidizable form [Eq. (24)].

[11] The mechanism of the two-electron reduction of arylpalladium(II) complexes [7 a] taking place at wave R$_1$ has never been described in detail. However, since a two-electron direct reduction can be discounted, this reduction certainly proceeds through an EE- or ECE-based mechanism [12], i.e., through the production of a short-lived arylpalladium(I) intermediate.

[12] A. J. Bard, L. R. Faulkner, *Electrochemical Methods*. Wiley, New York. **1980**.

[13] a) C. Amatore, E. Carré, A. Jutand, unpublished results (**1995**). b) It was noted by one referee that the smaller size of wave O$_2$ in DMF relative to THF is consistent with the existence of equilibrium (9) in DMF. Indeed, both equilibria (i.e., Eqs. (6) or (9)) are expected to be displaced toward their right-hand side in DMF relative to THF, owing to a stronger stabilization of low-coordinate palladium(0) moieties in DMF.

[14] a) J. F. Fauvarque, F. Pflüger, M. Troupel, *J. Organomet. Chem.* **1981**, *208*, 419. b) C. Amatore, F. Pflüger, *Organometallics* **1990**, *9*, 2276.

[15] This should be compared to the increased basicity of electrogenerated bases (i.e., B$^-$NR$_4^+$) relative to their usual analogues (i.e., [B$^-$M$^+$], M = Li, Na, K, etc.). For reactivity of electrogenerated bases, see e.g., M. Baizer, *Organic Electrochemistry* (Eds.: H. Lund, M. Baizer), Dekker, New York. **1991**. Chap. 30, pp. 1265–1277.

[16] For a review, see e.g. D. G. Peters, *Organic Electrochemistry*, (Eds.: H., Lund, M., Baizer), Dekker, New York. **1991**. Chap. 7, pp. 331–359.

[17] The fact that two-electron waves are observed for the reduction of aryl halides (i.e. ThI or PhI here) establishes that the σ-aryl anion does not react with its precursor. Indeed, such a father–son process would correspond to a one-electron overall stoichiometry [18].

[18] Compare e.g. C. Amatore, G. Capobianco, G. Farnia, G. Sandonà, J. M. Savéant, M. G. Severin, E. Vianello, *J. Am. Chem. Soc.* **1985**, *107*, 1815, and references therein.

[19] As established by comparison with the independent cyclic voltammetry ($E^p = -2.60$ V vs. SCE at 0.5 Vs^{-1}) of an authentic sample of 2-phenylthiophene prepared according to ref. [3 e].

[20] One could also conceive that Ar–Pd^{0}L$_2^-$ or the σ-aryl anion formed in Equation (6) act as a nucleophile in the reaction with the Ar–Pd^{II}XL$_2$ starting material [Eqs. (1,2)] [1,2]. However, this would lead to an overall one-electron consumption during the reduction of Ar–Pd^{II}XL$_2$ because of this father–son mechanism [18], in contradiction with the experimental two-electron stoichiometry [7 a]. We believe that the expected facile reaction of σ-phenyl anions with Ar–Pd^{II}XL$_2$ is prevented by their rapid protonation. However, this reaction can be observed when Ar$^-$ is a 2-thienyl anion and Ar–Pd^{II}XL$_2$ a phenyl derivative. Thus, by generating Th$^-$ by electrochemical reduction of 2-iodothiophene [Eqs. (13–15)] in the presence of the less readily reduced Ph–Pd^{II}XL$_2$, one observes a significant formation of 2-phenylthiophene [19] in cyclic voltammetry at small scan rates (ca. 50% yield at 0.2 Vs^{-1}; i.e., $t_{1/2} \approx 1.5$ s for the formation of 2-phenylthiophene). The formation of 2-phenylthiophene proceeds along a two-step sequence, at least, since the reaction of Th$^-$ is faster ($t_{1/2} \approx 0.5$ s) than the production of 2-phenylthiophene. Yet, even in this favorable case, the nucleophilic substitution of Ph–Pd^{II}XL$_2$ is too slow to compete efficiently with the oxidative addition of Ar′X and Ar–Pd^{0}L$_2^-$, which occurs much more rapidly, as has been shown in the present study. Indeed, from the values reported in Table 3, $t_{1/2}$ for the the reaction between Ar–Pd^{0}L$_2^-$ and aryl halides lies in the range between $7/n$ and $15/n$ milliseconds, where n is the number of equivalents of added aryl halide. So even in the least favorable case ($n = 1$) this reaction is at least thirty times faster than the nucleophilic substitution of the parent Ar–Pd^{II}XL$_2$ by aryl anions. This latter reaction should nevertheless become the major route for homo- or cross-coupling whenever the aryl halide is more easily reducible than Ar–Pd^{II}XL$_2$.

[21] In the presence of triphenylphosphine, the sequence in Equations (6 + 7 + 11) is kinetically equivalent to a first-order decomposition of the arylpalladium(0) anionic species; the rate determining step is the forward reaction in Equation (6) (rate constant k_0). Indeed, under these conditions, the rapid interception of the Pd^{0}L$_2$ moiety by the triphenylphosphine ligand [Eq. (11)] [8] opposes the facile backward recombination in Equation (6) [7a]. For this reason, the sequence of reactions (6 + 7 + 11) can be represented in Scheme 2 by its kinetically equivalent first-order process, with a rate constant k_0.

[22] Equation (16) and its integrated forms [Eqs. (17–19)] assume that the reactions between the aryl halide and the arylpalladium(0) anionic complexes are first-order in each reactant. The validity of this hypothesis is provided by the experimental observation of linear relationships when $\ln(i_0/i)$ is plotted as a function of $[\mathrm{Ar'X}]/v$ (compare Eq. (19) and Fig. 4 a), since ΔE is constant for the series of measurements.

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[23] This is required to ensure the constancy of the function $\mathcal{A}$ in Equations (17) and (18) (see Experimental Section).

[24] C. Amatore, A. Jutand, A. Suarez, *J. Am. Chem. Soc.* **1993**, *115*, 9531.

[25] a) *trans*-Bisarylpalladium(II) complexes are not supposed to undergo direct reductive elimination, yet, since this step was not investigated kinetically in this work, we preferred to formulate it as a global reaction. For the involvement of bisarylpalladium(II) complexes in palladium-catalyzed biaryl synthesis and their ability to undergo facile reductive elimination of biaryls, see refs. [1–2] and G. W. Parshall, *J. Am. Chem. Soc.* **1974**, *96*, 2360; E.-I. Negishi, T. Takahashi, K. Akiyoshi, *J. Organomet. Chem.* **1987**, *334*, 181. b) Such intermediates are expected to be reducible. However, in this study, examination of the reductive side of the voltammograms was hampered because of the excess of iodobenzene or *para*-substituted iodobenzene under our experimental conditions. c) Since we have no structural information on the bisarylpalladium(II) intermediate, we postulate that this is a classical *trans* complex only to remain in agreement with previous authors (see [25a]). This species may, however, be, for example, a *cis* complex or a solvent-coordinated neutral pentacoordinate species [24]. Note that our conclusion must remain true because of stoichiometry, even when the final product of Scheme 4 is not a classical bisarylpalladium(II) complex.

[26] This was ascribed to a facile CE electrochemical process: indeed, the fast, but up-hill dissociation of one halide ion ligand from $Ar{-}Pd^{II}XX'L_2^-$ affords $Ar{-}Pd^{II}YL_2$ ($Y = X$ or X'), which is reducible at this potential [24].

[27] The yields of homo- or heterocoupling products were less than 10%, and a few percent of products resulting from coupling with the phenyls borne by the phosphine ligands were also produced. Moreover, most of the aryl halides reactants underwent reduction. This indicates that the palladium catalyst is rapidly decomposed when the reaction is performed on a preparative scale in THF. The same occurs when the reaction is performed in a batch procedure in THF (compare Table 1, last row, in DMF).

[28] a) For the reaction of $Ar_2Pd^{II}L_2$ complexes with strong nucleophilic bases, see e.g. H. Nakazawa, F. Ozawa, A. Yamamoto, *Organometallics* **1983**, *2*, 241. For recent publications on scrambling reactions in the decomposition of $Ar{-}Pd^{II}YL_2$ complexes, see e.g.: b) B. E. Segelstein, T. W. Butler, B. L. Chenard, *J. Org. Chem.* **1995**, *60*, 12 c) K. C. Kong, C. H. Cheng, *J. Am. Chem. Soc.* **1991**, *113*, 6313.

[29] D. T. Rosevear, F. G. Stone, *J. Chem. Soc. A* **1968**, 164.

[30] a) P. Fitton, M. P. Johnson, J. E. Mc Keon, *J. Chem. Soc. Chem. Commun.* **1968**, 6. b) D. R. Coulson, *ibid.* **1968**, 1530. c) P. Fitton, E. A. Rick, *J. Organomet. Chem.* **1971**, *28*, 287.

[31] C. Amatore, M. Azzabi, P. Calas, A. Jutand, C. Lefrou, Y. Rollin, *J. Electroanal. Chem.* **1990**, *288*, 45.

[32] δ values depend on the duration $\Delta E/v$ of the overall electrochemical experiment: $\delta \propto (D\Delta E/v)^{1/2}$ [12]. Yet, for a given experiment, δ is a constant term since D, ΔE, and v are constant. This allows straight divisions by δ to be performed under derivative and integral operators.

[33] β, an adjustable parameter whose value is close to unity, is introduced to account for the finite widths of the waves. Indeed, because of these finite widths, the electrogeneration of $Ar{-}Pd^0L_2^-$ is not instantaneous. It starts before the peak of wave R_1 is reached, and carries on after this peak has been scanned; similarly, its detection begins before that of wave O_2 is reached and is not complete after this peak is scanned. The real reaction time to be considered is therefore not $\Delta E/v$, but $\beta\Delta E/v$. An average value $\beta = 0.97$ has been evaluated empirically by using simulations based on an ECEC mechanism with average ΔE and half-peak widths values comparable to those found in this study (cf. Fig. 1).