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Nickel- and Palladium-Catalyzed Homocoupling of Aryl Triflates. Scope, Limitation, and Mechanistic Aspects

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Whereas the direct reduction of aryl triflates affords mainly phenols and some arenes, the presence of a catalytic amount of palladium or nickel results in the formation of biaryls. The homocoupling is performed in the presence of an electron source, either a cathode or zinc powder. A judicious choice of the metal (nickel or palladium), the ligand (monodentate or bidentate phosphine), and the reduction process (electrochemical or chemical) allows the synthesis of functional symmetrical biaryls. Nickel and palladium complexes ligated by bidentate ligands such as $NiCl_2$(dppf) and $Pd(OAc)_2 + 1$ BINAP are very efficient for the homocoupling of 1-naphthyl triflate, since the dimer was obtained in almost quantitative yield. However, the homocoupling is sensitive to steric hindrance, excluding for the moment the synthesis of atropisomers. The homocoupling proceeds *via* an activation of the C−O bond of the aryl triflate by a palladium(0) (or a nickel(0)) complex, providing an intermediate arylpalladium(II) (or nickel(II)) complex that after activation by electron transfer affords a new complex able to undergo a second oxidative addition with the aryl triflates.

Introduction

Biaryls exhibit a large variety of physical and chemical properties.[1] When unsymmetrically substituted by donor and acceptor groups, they are used as materials for nonlinear optics.[2] They are also precursors of rigid liquid crystals.[3] Moreover, they can be used as redox mediators.[4] When substituted in the *ortho* and *ortho′* position, they form atropisomers and therefore are employed as chiral ligands for asymmetric syntheses.[1,5] Some natural biaryls have biological activity.[1]

Biaryls[1,6] are usually synthesized from aryl halides, either in the presence of a stoichiometric amount of copper (Ullmann reaction)[6a]

$$2ArX + Cu \rightarrow Ar{-}Ar + CuX_2$$

or *via* two reactions, catalyzed by a nickel or palladium catalyst: cross-coupling (eq 1) between aryl halides and aryl nucleophiles (Grignard,[5a,b,7,8] organozinc,[2c,e,f,8,9] aluminum,[9] stannane,[10] or borane[11] derivatives) or homocoupling (eq 2) of aryl halides in the presence of a chemical reductant[12] or of the electrons provided by a cathode.[13]

$$ArX + Ar'm \xrightarrow{\text{Pd or Ni}} Ar{-}Ar' + mX \qquad (1)$$

$$2\,ArX + 2e\ (\text{or Zn}) \xrightarrow{\text{Pd or Ni}} Ar{-}Ar + 2X^-\ (\text{or } ZnX_2) \qquad (2)$$

The cross-coupling allows the synthesis of symmetrical and unsymmetrical biaryls, whereas the homocoupling is restricted to the synthesis of symmetrical ones. However, the homocoupling takes the advantageous of by-

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passing the synthesis of aryl nucleophiles, which sometimes requires two steps (*e.g.*, synthesis of an aryl Grignard or aryllithium reagent followed by exchange with a zinc,[2c,8] borane[11] or stannane[10] derivative). Moreover, the formation of arylmagnesium or lithium reagents may be not compatible with functional groups substituted on the aryl ring. Many syntheses of biaryls have been achieved by the cross-coupling reaction, and since 1987, this reaction was widely developed from aryl triflates.[14]

$$\mathrm{ArOTf} + \mathrm{Ar'm} \xrightarrow{\text{Pd or Ni}} \mathrm{Ar{-}Ar'} + \mathrm{mOTf} \qquad (3)$$

Indeed, it has been shown that palladium(0) or nickel(0) complexes activate the Ar−O bond of aryl triflates *via* an oxidative addition, which produces arylpalladium[14o,15] or arylnickel intermediates prone to react with nucleophiles. In 1992, we demonstrated that it was possible to invert the reactivity of aryl triflates and make them react with electrophiles such as carbon dioxide (synthesis of aryl carboxylic acids)[16] or the aryl triflate itself (synthesis of biaryls),[16] provided the presence of a palladium catalyst and a source of electrons supplied by a cathode (eq 4).

$$2\mathrm{ArOTf} + 2\mathrm{e} \xrightarrow{\text{Pd}} \mathrm{Ar{-}Ar} + 2\mathrm{TfO}^- \qquad (4)$$

In 1993, we extended the scope of the palladium-catalyzed homocoupling of aryl triflates with zinc powder as the electron source and with nickel catalysts associated to bidentate ligands (eq 5).

$$2\mathrm{ArOTf} + \mathrm{Zn} \xrightarrow{\text{Pd or Ni}} \mathrm{Ar{-}Ar} + \mathrm{Zn(OTf)_2} \qquad (5)$$

The great accessibility of aryl triflates from easily available phenols[19] makes them competitive with aryl iodides or bromides. We wish now to report more details on the scope, the limitation, and the mechanism of the palladium- and nickel-catalyzed homocoupling of aryl triflates.

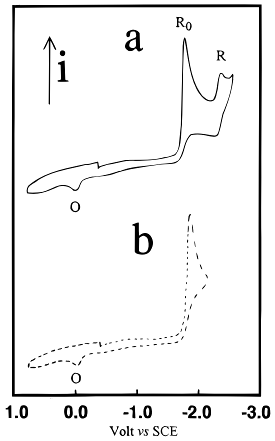

Figure 1. (a) Cyclic voltammetry of 1-naphthyl triflate (2 mM) in DMF (0.3 M *n*-Bu$_4$NBF$_4$) at a stationary gold disk electrode (∅ = 0.5 mm) with a scan rate of 0.2 V s^{-1}, at 20 °C. (b) The cyclic voltammetry was performed in the same conditions as in (a) but the potential was reversed just after the reduction peak R$_0$.

Results and Discussion

Electrochemical Properties of Aryl Triflates, Alone and in the Presence of PdCl$_2$(PPh$_3$)$_2$ in DMF. Aryl triflates are electroactive compounds.[20] The cyclic votammogram of aryl triflates, 2 mM in DMF containing *n*-Bu$_4$NBF$_4$ (0.3 M) as supporting electrolyte, exhibited an irreversible reduction peak. See, for example, the reduction peak R$_0$ of 1-naphthyl triflate in Figure 1a.

The electrochemical reduction of 1-naphthyl triflate at $E^{\mathrm{p}}{}_{\mathrm{R0}} = -1.95$ V produced some naphthalene (formed by fast protonation of the 1-naphthyl anion), characterized by its reversible reduction peak at $E^{\mathrm{p}}{}_{\mathrm{R}} = -2.51$ V (Figure 1a) and 1-naphthoxide detected on the reverse scan, by its irreversible oxidation peak[21] at $E^{\mathrm{p}}{}_{\mathrm{O}} = -0.07$ V (Figure 1a,b).

$$\mathrm{ArOTf} + 2\mathrm{e} \rightarrow \mathrm{Ar}^- + \mathrm{TfO}^- \quad \mathrm{R_0} \qquad (6)$$

$$\mathrm{Ar}^- + \mathrm{H}^+ \rightarrow \mathrm{ArH} \qquad (7)$$

$$\mathrm{ArH} + 1\mathrm{e} \rightarrow \mathrm{ArH}^{\bullet -} \quad \mathrm{R} \qquad (8)$$

$$\mathrm{ArOTf} + 2\mathrm{e} \rightarrow \mathrm{ArO}^- + \mathrm{Tf}^- \quad \mathrm{R_0} \qquad (9)$$

$$\mathrm{ArO}^- \rightarrow \mathrm{ArO}^\bullet + 1\mathrm{e} \quad \mathrm{O} \qquad (10)$$

Reactions 6 and 9 proceed *via* a common intermediate formed by the first electron transfer:

$$\mathrm{ArOTf} + 1\mathrm{e} \rightarrow \mathrm{ArOTf}^{\bullet -} \quad \mathrm{R_0} \qquad (11)$$

This intermediate radical anion, ArOSO$_2$CF$_3$$^{\bullet -}$, evolves by either cleavage of the C−O bond

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[18] (a) A dimerization of aryl triflates was reported to be efficient only under ultrasonication and limited to NiCl$_2$(PPh$_3$)$_2$ as catalyst, used with a large excess of PPh$_3$, which makes the workup more complicated. See: (b) Yamashita, J.; Inoue, Y.; Kondo, T.; Hashimoto, H. *Chem. Lett.* **1986**, 407. (c) A NiCl$_2$(PPh$_3$)$_2$-catalyzed polymerization of aryl bis(triflates) was also reported. See: Persec, V.; Okita, S.; Weiss, R. *Macromolecules* **1992**, *25*, 1816.

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[20] To our knowledge the electrochemical reduction of aryl triflates is not reported. The electrochemical reduction of aryl tosylates affords mainly phenols. See: Civitello, E. R.; Rapoport, H. *J. Org. Chem.* **1992**, *57*, 834.

[21] For the electrochemical oxidation of phenoxides see: Hapiot, P.; Pinson, J.; Yousfi, N. *New J. Chem.* **1992**, *16*, 877.

$$ArOTf^{\bullet -} \rightarrow Ar^{\bullet} + TfO^{-} \qquad (12)$$

or cleavage of the O-S bond

$$ArOTf^{\bullet -} \rightarrow ArO^{\bullet} + Tf^{-} \qquad (13)$$

These reactions are followed by the reduction of the aryl or aryloxy radical at a potential less negative than that of the starting compound ArOTf

$$Ar^{\bullet} + 1e \rightarrow Ar^{-} \qquad E < E_{R0} \qquad (14)$$

$$ArO^{\bullet} + 1e \rightarrow ArO^{-} \qquad E' < E_{R0} \qquad (15)$$

and thus, the overall process is a two-electron transfer occurring at the potential of R_0 (eqs 6 and 9).

The reduction peak potentials of some aryl triflates, determined *vs* SCE at a gold electrode, with a scan rate of 0.2 V s^{-1}, are collected in Table 1.

As expected, aryl triflates are more easily reduced when substituted by electron-withdrawing groups. They are reduced at more negative potentials than the corresponding aryl iodides but are more easily reduced than aryl bromides and chlorides: compare $E^{p}_{Red} = -2.10$, -2.63, -2.70, >-2.80 V for, respectively, PhI, PhOTf, PhBr, and PhCl.

An exhaustive electrolysis conducted on a solution of 1 mmol of 1-naphthyl triflate in DMF (50 mL), at the controlled potential of -2 V, afforded mainly the 1-naphthol (86%)[16] and a small amount of naphthalene (13%), demonstrating that the cleavage of the O$-$S bond in the intermediate radical anion $ArOTf^{\bullet -}$ (eq 13) is highly favored compared to the cleavage of the C$-$O bond (eq 12), the corresponding $ArO^{\bullet}$ radical being more stable than $Ar^{\bullet}$. It is important to notice that the direct reduction of aryl triflates does not produce any dimer, *i.e.*, 1,1′-binaphthyl. The desired dimerization should thus be catalyzed by a transition metal complex able to activate the C$-$O bond of the aryl triflate such as palladium(0) or nickel(0) complexes.

The cyclic voltammogram of $PdCl_2(PPh_3)_2$, 2 mM, in DMF exhibited an irreversible reduction peak R_1 at -0.91 V (Figure 2). As already reported, the oxidation peak O_1 detected on the reverse scan at -0.03 V characterizes the electrogenerated anionic palladium(0) complex ligated by one chloride anion: $Pd^0(PPh_3)_2Cl^-$.[22]

$$Pd^{II}Cl_2(PPh_3)_2 + 2e \rightarrow Pd^{0}(PPh_3)_2Cl^{-} + Cl^{-} \qquad R_1 \qquad (16)$$

When the reduction of the bivalent palladium was performed in the presence of increasing amounts of 1-naphthyl triflate, we observed that the magnitude of the oxidation peak O_1 of $Pd^0(PPh_3)_2Cl^-$ progressively decreased (Figure 2), demonstrating that the electrogenerated palladium(0) complex reacted with the aryl triflate. We recently established that oxidative addition of aryl triflates with a palladium(0) complex such as $Pd^0(PPh_3)_4$ did not afford a neutral complex $ArPd(OTf)(PPh_3)_2$ but a cationic arylpalladium(II) complex $ArPd(PPh_3)_2^+$, with TfO^- as the counteranion, due to the poor affinity of the triflate anion for the palladium(II) center.[15] However, a neutral complex *trans*-$ArPdCl(PPh_3)_2$ was formed when the oxidative addition was performed in the presence of chloride anions.[15] Therefore, in the present case, the oxidative addition leads to a neutral arylpalladium complex $ArPdCl(PPh_3)_2$ (eq 17).

Table 1. Reduction Peak Potentials of Aryl Triflates and of the Arylpalladium(II) Complexes Resulting from the Oxidative Addition

$Pd^0(PPh_3)_2Cl^- + ArOTf \rightarrow ArPdCl(PPh_3)_2 + TfO^-$

Ar$-$	ArOTf, E^{p}_{Red} [a]	$ArPdCl(PPh_3)_2$, E^{p}_{Red} [a]
p-$MeCOC_6H_4-$	-1.68	-1.65
p-CNC_6H_4-	-1.80	-1.75
$TfOC_6H_4-$	-2.24	-2.15
p-$CF_3C_6H_4-$	-2.21	-2.00
p-ClC_6H_4-	-2.50	-2.41
o-ClC_6H_4-	-2.45	-2.20
p-FC_6H_4-	-2.54	-2.54
C_6H_5-	-2.63	-2.20
o-MeC_6H_4-	-2.70	-2.46
p-MeC_6H_4-	-2.71	-2.53
p-$MeOC_6H_4-$	-2.67	*b*
p-$tBuC_6H_4-$	-2.74	-2.68
1-naphthyl$-$	-1.95	-1.89, -2.35 [c]
2-naphthyl$-$	-2.01	nd
2-pyridyl$-$	-2.12	-2.00

[a] Volt *vs* SCE. Reduction peak potentials were determined at a steady gold disk electrode at the scan rate of 0.2 V s^{-1}, in DMF containing n-Bu_4NBF_4 (0.3 M), 20 °C. [b] No reaction [c] The ligand on the palladium was n-Bu_3P.

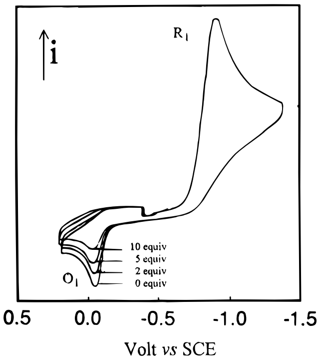

Figure 2. Cyclic voltammetry of $PdCl_2(PPh_3)_2$ (2 mM) in DMF (0.3 M n-Bu_4NBF_4) at a stationary gold disk electrode (∅ = 0.5 mm) with a scan rate of 0.2 V s^{-1}, at 20 °C. Variation of the oxidation peak current O_1 of the electrogenerated palladium(0) complex in the presence of 1-naphthyl triflate, successively 0, 4, 10, and 20 mM.

$$Pd^{0}(PPh_3)_2Cl^{-} + ArOTf \rightarrow ArPdCl(PPh_3)_2 + TfO^{-} \qquad (17)$$

It has been established that the oxidative addition of aryl iodides with the electrogenerated $Pd^0(PPh_3)_2Cl^-$ complex afforded the *trans*-complex $ArPdI(PPh_3)_2$ *via* a pentacoordinated anionic complex $ArPdICl(PPh_3)_2^-$, detected and characterized by its oxidation peak located at a more positive potential than that of O_1.[23] Due to the

$$Pd^{0}(PPh_3)_2Cl^{-} + ArI \rightarrow ArPdICl(PPh_3)_2^{-} \rightarrow \cdot\cdot \rightarrow \textit{trans}\text{-}ArPdI(PPh_3)_2 + Cl^{-} \qquad (18)$$

very low affinity of the triflate anion for the palladium(II) center,[15] the formation of a stable pentacoordinated anionic intermediate complex such as $ArPd(OTf)Cl(PPh_3)_2^-$ is less probable, and actually no oxidation peak that could have characterized such a pentacoordinated species was

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Table 2. Comparative Reactivity of Palladium(0) Complexes in their Oxidative Addition with 1-Naphthyl-OTf in DMF at 20 °C

Pd^0	k_{app} (M^{-1} s^{-1})	Pd^0	k_{app} (M^{-1} s^{-1})
$Pd^0(PPh_3)_4$	7.5×10^{-2}	$Pd^0(PPh_3)_2Cl^-$ ↑ $[Pd^{II}Cl_2(PPh_3)_2 + 2e]$	5.5
$Pd^0(PPh_3)_4$ + $150Cl^-$ [a]	4.3×10^{-1}		

[a] Introduced as n-Bu_4NCl.

detected on the reverse scan at the time scale of the cyclic voltammetry. This means that were the complex $ArPd(OTf)Cl(PPh_3)_2^-$ initially formed in the oxidative addition, its half-life time would be considerably smaller than that of $ArPdICl(PPh_3)_2^-$.

The rate constant of the oxidative addition of $Pd^0(PPh_3)_2Cl^-$ with the 1-naphthyl triflate was estimated by cyclic voltammetry[24] and compared to that of $Pd^0(PPh_3)_4$ alone[15] or in the presence of chloride anions.[15] The results collected in Table 2 show that, as expected,[22] the palladium(0) complex $Pd^0(PPh_3)_2Cl^-$, generated by reduction of $PdCl_2(PPh_3)_2$, is the most reactive complex because it is ligated by one chloride and by only two phosphines.

Therefore, since the oxidative addition of aryl triflates with palladium(0) complexes is slow compared to that of aryl iodides,[25] the use of $PdCl_2(PPh_3)_2$ as a precursor of a reactive palladium(0) complex able to activate aryl triflates is highly recommended. But even with this very reactive palladium(0) complex, its oxidative addition with 10 equiv of 1-naphthyl triflate was not complete at 20 °C, during the time scale of the cyclic voltammetry (9 s at the scan rate of 0.20 V s^{-1}) since the oxidation peak O_1 of $Pd^0(PPh_3)_2Cl^-$ remained partially present, as shown in Figure 2. To observe a faster oxidative addition, the reduction of $PdCl_2(PPh_3)_2$ was performed in the presence of a more reactive compound: p-$CF_3C_6H_4OTf$ [15] and at a smaller scan rate 0.05 V s^{-1}, which means during a longer time (38 s). Under these conditions, the oxidative addition of the electrogenerated $Pd^0(PPh_3)_2Cl^-$ with 1 equiv of p-$CF_3C_6H_4OTf$ was total, as attested by the absence of the oxidation peak O_1 on the reverse scan (Figure 3a).

When the reduction scan was performed at more negative potential than that of $PdCl_2(PPh_3)_2$ (R_1), a new reduction peak R_2 appeared at −1.90 V, *i.e.* at a less negative potential than that of p-$CF_3C_6H_4OTf$, R_0 at −2.12 V (Figure 3b). This new reduction peak R_2 is assigned to the reduction of the arylpalladium(II) complex p-$CF_3C_6H_4PdCl(PPh_3)_2$ resulting from the oxidative addition.

$$Pd^{II}Cl_2(PPh_3)_2 + 2e \rightarrow Pd^0(PPh_3)_2Cl^- + Cl^- \quad R_1 \qquad (16)$$

$$Pd^0(PPh_3)_2Cl^- + p\text{-}CF_3C_6H_4OTf \rightarrow p\text{-}CF_3C_6H_4PdCl(PPh_3)_2 + TfO^- \qquad (19)$$
$$\downarrow + e, R_2$$

The formation of a neutral complex $ArPdCl(PPh_3)_2$ was then definitively established by comparing the reduction peak potential (−1.91 V) of p-$CF_3C_6H_4PdCl(PPh_3)_2$, generated by reaction of $Pd^0(PPh_3)_4$ with p-$CF_3C_6H_4OTf$ in the presence of 1 equiv of chloride ions[15] and that of the electrogenerated one, detected at R_2 (−1.90 V).

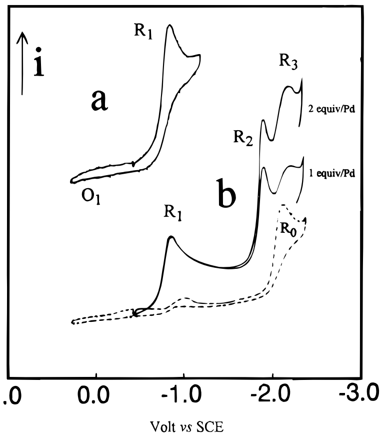

Figure 3. (a) Cyclic voltammetry of $PdCl_2(PPh_3)_2$ (2 mM) in DMF (0.3 M n-Bu_4NBF_4) in the presence of p-$CF_3C_6H_4OTf$ (2 mM) at a stationary gold disk electrode (∅ = 0.5 mm) with a scan rate of 0.05 V s^{-1}, at 20 °C. The current has been multiplied by a factor 2 when compared to (b). (b) (- - -) Cyclic voltammetry of p-$CF_3C_6H_4OTf$ (2 mM) alone. (—) Cyclic voltammetry of a mixture of $PdCl_2(PPh_3)_2$ (2 mM) and p-$CF_3C_6H_4$-OTf successively 2 and 4 mM.

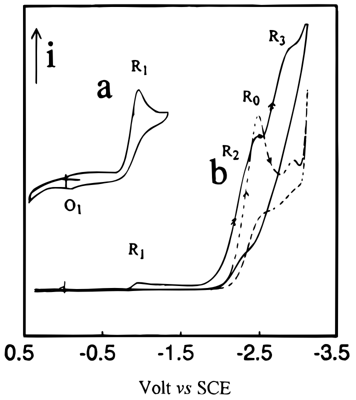

Figure 4. Cyclic voltammetry performed under the experimental conditions of an electrolysis. (a) Cyclic voltammetry of $PdCl_2(PPh_3)_2$ (2 mM) in DMF (0.1 M n-Bu_4NBF_4) in the presence of o-ClC_6H_4OTf (20 mM) at a stationary gold disk electrode (∅ = 0.5 mm) with a scan rate of 0.2 V s^{-1}, at 20 °C. The current has been multiplied by a factor 10 when compared to (b). (b) (- - -) Cyclic voltammetry of o-ClC_6H_4OTf (20 mM) alone. (—) Cyclic voltammetry of a mixture of $PdCl_2(PPh_3)_2$ (2 mM) and o-ClC_6H_4OTf (20 mM).

The reduction peak current R_2 grew when the concentration of the aryl triflate increased, demonstrating that peak R_2 was "catalytic". This demonstrates that the reduction of the arylpalladium(II) complex performed in the presence of the aryl triflate affords a new compound and a palladium(0) complex able to activate again the aryl triflate in a second catalytic cycle and so on. On the same voltammogram, at more negative potential, another reduction peak R_3 was detected at −2.18 V. The magnitude of this peak increased in the presence of an authentic sample of the dimer 4,4′-$CF_3C_6H_4C_6H_4CF_3$, demonstrating that R_3 is the reduction peak of the dimer. The same behavior was observed for another aryl triflate o-ClC_6H_4OTf (less reactive than p-$CF_3C_6H_4OTf$) as shown in Figure 4.

The reduction of $PdCl_2(PPh_3)_2$ performed in the presence of 10 equiv of o-ClC_6H_4OTf also resulted in the

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(24) For the determination of rate constants by cyclic voltammetry see ref 22.

(25) PhOTf was found to be 10^4 times less reactive than PhI and 1.7 times more reactive that PhBr.[15]

formation of the catalytic peak R_2 at −2.20 V while the reduction peak R_0 of the aryl triflate at −2.45 V had almost completely disappeared.

Therefore, the electrogenerated palladium(0) complex $Pd^0(PPh_3)_2Cl^-$ activates aryl triflates to afford neutral complexes $ArPd^{II}Cl(PPh_3)_2$ more easily reduced than the starting aryl triflates. Dimerization occurs after activation of the arylpalladium(II) complex by electron transfer, with regeneration of the initial palladium(0) complex. It

$$\mathrm{ArPdCl(PPh_3)_2 + 2e + ArOTf \rightarrow Ar{-}Ar + Pd^0(PPh_3)_2Cl^- + TfO^-} \tag{20}$$

is reported that the reduction of arypalladium(II) complexes affords an anionic $ArPd^0(PPh_3)_2^-$ species according to the following reactions:[26]

$$\mathrm{ArPdCl(PPh_3)_2 + 2e \rightarrow ArPd^0(PPh_3)_2^- + Cl^-} \tag{21}$$

$$\mathrm{ArPd^0(PPh_3)_2^- \rightleftarrows Ar^- + Pd^0(PPh_3)_2} \tag{22}$$

The mechanism of the palladium-catalyzed electrodimerization of aryl iodides has been elucidated, and the key step was found to be the oxidative addition of the anionic arylpalladium(0) complex $ArPd^0(PPh_3)_2^-$ with the aryl iodide, affording a transient pentacoordinated species[13e]

$$\mathrm{ArPd^0(PPh_3)_2^- + ArX \rightarrow Ar_2Pd^{II}X(PPh_3)_2^- \rightarrow Ar_2Pd^{II}(PPh_3)_2 + X^-} \tag{23}$$

followed by reductive elimination:

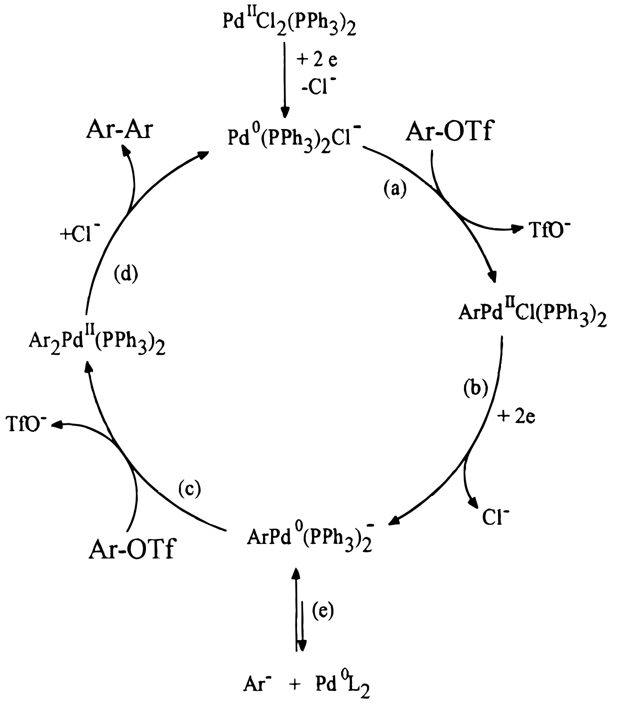
$$\mathrm{Ar_2Pd^{II}(PPh_3)_2 \rightarrow Ar{-}Ar + Pd^0(PPh_3)_2} \tag{24}$$

Since the intermediate complex $ArPdCl(PPh_3)_2$ was identified when starting from aryl triflates, the palladium-catalyzed electrodimerization of aryl triflates should proceed by a similar mechanism except that the low affinity of triflate anion for palladium(II) center[15] in DMF excludes the formation of anionic palladium(II) complexes ligated by a triflate anion. Therefore, the mechanism of the palladium catalyzed electrodimerization of aryl triflates can be described as shown in Scheme 1.

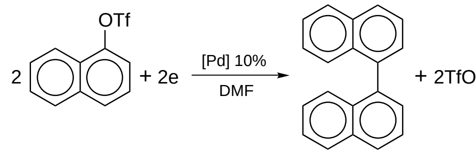
This mechanistic approach of the palladium-catalyzed electrodimerization of aryl triflates investigated by cyclic voltammetry allows the determination of the reduction potentials of the intermediate arylpalladium(II) complexes, $ArPdCl(PPh_3)_2$, *i.e.*, the potentials at which the electrolyses should be conducted to produce biaryl. The reduction potentials of some $ArPdCl(PPh_3)_2$ intermediates formed *via* the oxidative addition are collected in Table 1. In every case these complexes are more easily reduced than the precursor aryl triflate. This is a strict condition for the formation of biaryl. In some cases, the difference between the two potentials is small (Table 1) but we will see later on that it is high enough to ensure the success of the dimerization, provided the electrosyntheses were carried out at controlled potentials.

In order to enhance the rate of the oxidative addition, $PdCl_2(n\text{-}Bu_3P)_2$ was used as a precursor of a more reactive palladium(0) complex. However, the complex resulting from its oxidative addition with the 1-naphthyl triflate, *i.e.*, 1-naphthyl-$PdCl(n\text{-}Bu_3P)_2$, was found to be reduced at a more negative potential than that of the 1-naphthyl triflate (Table 1), excluding the use of $PdCl_2(n\text{-}Bu_3P)_2$ as a catalyst for the homocoupling.

Scheme 1



Palladium-Catalyzed Electrosynthesis of Biaryls from Aryl Triflates. The reaction was first tested on the 1-naphthyl triflate:



(25)

The electrolyses were carried out in DMF, in a divided cell, at controlled potential, until the electrolysis current dropped to 5% of its initial value. The results of the electrolyses are collected in Table 3.

Whereas in the absence of any catalyst, no dimer was formed (Table 3, entry 1), the addition of a catalytic amount of a palladium catalyst resulted in the formation of 1,1′-binaphthyl, at a less negative potential than the reduction potential of the 1-naphthyl triflate. The dimerization was very sensitive to the temperature, and by comparing entries 2−5 (Table 3), we observed that the best yield in dimer was obtained at 90 °C. A higher temperature resulted in a lower yield probably due to decomposition of the catalytic species. Some 1-naphthol was formed as a byproduct, but it could be easily converted back to the initial 1-naphthyl triflate. The formation of 1-naphthol can be limited by decreasing the value of the electrolysis potential (compare Table 3, entries 4 and 6). The dimerization was not efficient at low temperature, and a large amount of 1-naphthol was thus produced. This shows that the oxidative addition of the electrogenerated palladium(0) with the 1-naphthyl triflate was too slow at room temperature and that under these conditions the direct reduction of the 1-naphthyl triflate to the 1-naphthol could not be avoided and thus became preponderant.

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[26] Amatore, C.; Jutand, A.; Khalil, F.; Nielsen, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 7076.

Table 3. Electrosynthesis of 1,1′-Binaphthyl from 1-Naphthyl-OTf Catalyzed by Palladium Complexes (Eq 25)

n	1-naphthyl-OTf,[a] mmol	catalyst (10%)	E^b (V)	*T*, °C	ArAr,[c] %	ArH,[c] %	ArOH,[c] %
1	1	none	−2.0	20	0	13	86
2	1	$PdCl_2(PPh_3)_2$	−1.7	20	7	33	60
3	1	$PdCl_2(PPh_3)_2$	−1.7	60	40 (34)	33 (32)	28 (27)
4	1	$PdCl_2(PPh_3)_2$	−1.7	90	50	36	13
5	1	$PdCl_2(PPh_3)_2$	−1.7	120	36	42	22
6	1	$PdCl_2(PPh_3)_2$	−1.6	90	45	34	2[d]
7	10	$PdCl_2(PPh_3)_2$	−1.7	90	50	33	13
8	1	$PdCl_2(MePPh_2)_2$	−1.7	90	30	36	28
9	1	$PdCl_2(dppm)$	−1.7	90	35	33	26
10	1	$PdCl_2(dppe)$	−1.7	90	33	43	18
11	1	$PdCl_2(dppp)$	−1.7	90	31	46	21
			−1.4	90	35	50	11
12	1	$PdCl_2(dppb)$	−1.7	90	40	45	0

[a] Solvent: DMF, 50 mL containing *n*-Bu_4NBF_4 (0.3 M) as supporting electrolyte. [b] Electrolysis potential *vs* SCE. [c] Yields are relative to the initial 1-naphthyl-OTf that was completely converted and determined on the crude mixture, after workup, by ^1H NMR (250 MHz) spectroscopy, using $CHCl_2CHCl_2$ as internal standard. Isolated yields of pure products are given in parentheses. [d] 1-Naphthyl-OTf recovered: 18%.

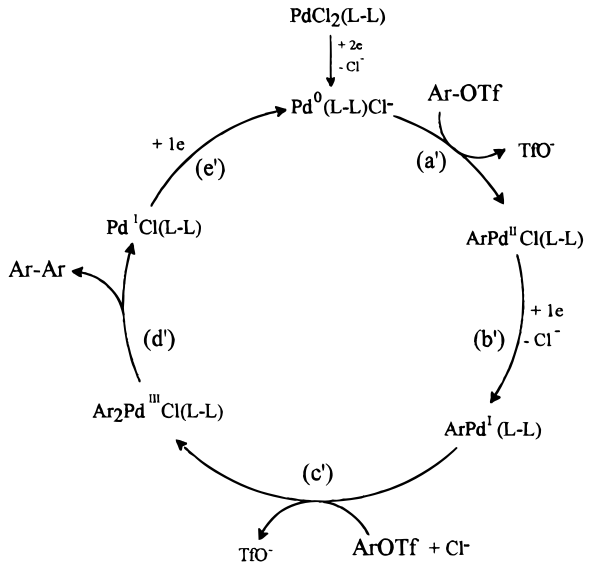
Table 4. Properties of Free and Ligated Phosphines

	phosphine pK_a[28]	phosphine cone angle,[30] deg	P−Pd−P bite angle,[31] deg
PPh_3	2.73	145	
$MePPh_2$	4.57	136	
dppm			72.7
dppe			85.8
dppp			90.6
dppb			> 90

The formation of naphthalene, a second byproduct, is more troublesome. The latter probably arose from protonation of the anion 1-naphthyl⁻ formed by reduction of the intermediate 1-naphthylpalladium(II) complex (see reactions b and e in Scheme 1). However, the origin of the proton is not clear.[27] Decreasing the amount of the supporting electrolyte *n*-Bu_4NBF_4, which might be a source of proton *via* an Hoffmann elimination or using $LiBF_4$ as the supporting electrolyte, did not improve the selectivity of the reaction, evidencing that the proton source was either the solvent or residual water. The use of TMU (tetramethylurea) did not improve the selectivity neither.

To get a better selectivity, a series of catalysts were tested, in which the palladium was ligated by either mono- or bidentate phosphines. Two oxidative additions (reactions a and c) and a reductive elimination (d) are involved in the mechanism described in Scheme 1. We do not know *a priori* what is the rate-determining step of the catalytic cycle. By using a more basic phosphine than PPh_3 such as $MePPh_2$ (see their respective pK_a values[28] in Table 4), we expected faster oxidative additions[29a,b] and a slower reductive elimination.[29c] The fact that the yield in dimer was lower (compare Table 3, entries 4 and 8) tends to prove that the reductive elimination (d) is the rate-determining step of the catalytic cycle. This hypothesis was confirmed when the respective cone angles of these two phosphines were considered[30] (Table 4). A less bulky phosphine such as $MePPh_2$ should favor the oxidative addition but should disfavor the reductive elimination.[29d]

Scheme 2



When the palladium was ligated by bidentate ligands (Table 3, entries 9−12), the yield in dimer was lower compared to that obtained with PPh_3 as ligand, and the 1-naphthol was formed in a higher amount due to a less efficient catalytic cycle. Since this is the first report of the dimerization of aryl derivatives catalyzed by palladium complexes ligated by bidentate ligands, the mechanism of the dimerization is not known. However, since PhPdX(dppe) complexes were found to be reduced by 1 electron,[26] the mechanism should be very similar to that of the $NiCl_2$(dppe)-catalyzed dimerization of aryl halides, in which only monoelectronic transfers are involved.[13d] Therefore, we propose the Scheme 2, in which L−L symbolizes a bidentate ligand.

Two oxidative additions (a′) and (c′) and a reductive elimination (d′) are involved in Scheme 2. In the case of bidentate ligands, we have to consider their P−Pd−P bite angle[31] (Table 4). Oxidative additions are supposed to be disfavored for high P−Pd−P angles, whereas the reductive eliminations are favored,[29d,e] the bulkiness of the ligand making the two aryl groups closer. In the

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(27) The palladium-catalyzed electroreduction of aryl triflates to arenes, in the presence of a proton source, has been recently reported. See: Chiarotto, I.; Cacchi, S.; Pace, P.; Carelli, I. *J. Electroanal. Chem.* **1995**, *385*, 235.

(28) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650.

(29) (a) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434. (b) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818. (c) Negishi, E. I.; Takahashi, T.; Akiyoshi, K. *J. Organomet. Chem.* **1987**, *334*, 181. (d) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (e) Brown, J. M.; Guiry, P. J. *Inorg. Chim. Acta* **1994**, *220*, 249.

(30) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Table 5. Electrosynthesis of Biaryls from Aryl Triflates Catalyzed by $PdCl_2(PPh_3)_2$ (Eq 26)

entry	ArOTf[a]	E,[b] V	ArAr,[c] % (isolated)	ArH,[c] %	ArOH,[c] %
1	p-CNC_6H_4OTf[d]	−1.5	4,4′-$CNC_6H_4C_6H_4CN$ 70 (55)	0	15
2	p-$CF_3C_6H_4OTf$[d]	−1.7	4,4′-$CF_3C_6H_4C_6H_4CF_3$ 68 (45)	0	5
3	p-ClC_6H_4OTf[d]	−1.8	4,4′-$ClC_6H_4C_6H_4Cl$ (57)	0	8
4	o-ClC_6H_4OTf[d]	−2.0	2,2′-$ClC_6H_4C_6H_4Cl$ (34)	0	26
5	C_6H_5OTf[d]	−2.0	$C_6H_5C_6H_5$ 30	nd	30
6	C_6H_5OTf[e]	−2.0	$C_6H_5C_6H_5$ 83 (76)	nd	10
7	p-$MeOC_6H_4OTf$[d]	−2.0	4,4′-$MeOC_6H_4C_6H_4OMe$ (15)	0	56
8	2-C_5H_4NOTf[d]	−1.4	2,2′-bipyridine (78)	0	0

[a] Solvent: DMF, 50 mL containing n-Bu_4NBF_4 (0.3 M) as supporting electrolyte. [b] Electrolysis potential *vs* SCE. [c] Yields are relative to the initial ArOTf that was completely converted and determined on the crude mixture, after workup, by ^1H NMR (250 MHz) spectroscopy, using $CHCl_2CHCl_2$ as internal standard. [d] 1 mmol of ArOTf with 0.1 mmol of $PdCl_2(PPh_3)_2$. [e] 10 mmol of ArOTf with 1 mmol of $PdCl_2(PPh_3)_2$.

series of bidentate ligands tested (Table 3, entries 9−12), the highest yield in dimer was obtained for dppb, which possesses the highest P−Pd−P angle. This suggests that the reductive elimination (d′) is the rate-determining step of the catalytic cycle.[32]

Triphenylphosphine appears to be the best ligand for the electrosynthesis of 1,1′-binaphthyl. This reaction was scaled up from 1 to 10 mmol provided 10% of the catalyst was used (Table 4, entry 7). Indeed, when the percentage of the catalyst was decreased from 10 to 1%, the 1-naphthol was the major product (56%). In that case, the magnitude of the reduction wave of the 1-naphthyl triflate became much higher than that of the catalytic wave, and their respective reduction potentials (Table 1) are too close to avoid the direct reduction of the 1-naphthyl triflate to 1-naphthol.

The experimental conditions leading to the best yield in 1,1′-binaphthyl were used to synthesize biaryls according to reaction 26:

$$2\mathrm{ArOTf} + 2e \xrightarrow[\text{DMF, 90 °C}]{[\mathrm{PdCl_2(PPh_3)_2}],\ 10\%} \mathrm{Ar{-}Ar} + 2\mathrm{TfO}^- \qquad (26)$$

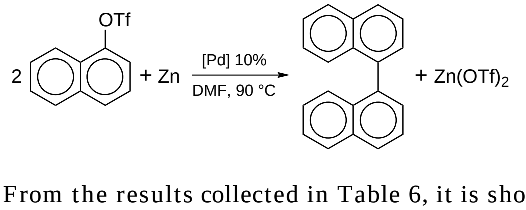
The electrolyses were performed under controlled potentials. The potential was always chosen slightly less negative than the reduction peak potential of the arylpalladium(II) intermediate (Table 1) to avoid the direct reduction of the aryl triflate. The results collected in Table 5 indicate that good yields in dimer were generally obtained when starting from phenyl triflates substituted in the *para* position by electron-withdrawing groups.

An aryl triflate substituted by an electron-donor group (OMe) was considerably less reactive. This proves that when the phenyl triflates were substituted by an electron-donor group, the oxidative addition of the palladium(0) with the aryl triflate was the rate-determining step. Indeed, we have already reported that the oxidative addition of *para*-substituted phenyl triflates with $Pd^0(PPh_3)_4$ follows a Hammett correlation with a positive value of ρ (+2.55), the oxidative addition being faster when the substituent is an electron-withdrawing group.[15]

The selectivity of the homocoupling was higher than in the case of the 1-naphthyl triflate, since no arene ArH was detected. The corresponding phenol was the only byproduct that was obtained in significant yield, only in the case of poorly reactive aryl triflates (those substituted in the *ortho* position or those substituted in the *para* position by electron-donor groups such as OMe). In those cases, the catalytic efficiency was low, and it was not possible to avoid the direct reduction of the aryl triflate to ArOH. The fact that lower yields in dimer were obtained from 1-naphthyl triflate or from phenyl triflates substituted in the *ortho* position indicates that the dimerization is sensitive to steric hindrance around the palladium.

In all cases, the homocoupling was regiospecific. It was compatible with functional groups substituted on the phenyl ring (CN, CF_3, Cl), except for NO_2, which was further reduced, leading to mixtures of biaryls containing the nitro group and/or the NH_2 group. The dimerization was successfully extended to heteroaromatic ring such as pyridyl.

Palladium- and Nickel-Catalyzed Synthesis of Biaryls from Aryl Triflates in the Presence of Zinc Powder as Reductant. We have established that the key step of the palladium-catalyzed electrochemical homocoupling of aryl triflates was the activation of an intermediate arylpalladium complex by electron transfer. Since easily oxidizable metals can supply electrons, zinc powder[12] was tested in a chemical homocoupling of aryl triflates, a process that is *a priori* more easily handled than the electrochemical one. The chemical process was first optimized on the 1-naphthyl triflate because its electrochemical homocoupling was limited to 50% yield and 1,1′-binaphthyls, when substituted in the 2,2′ positions, are good candidates for the formation of atropisomers.[5] Indeed, our purpose was to realize the enantioselective homocoupling of hindered aryl triflates, in the presence of catalysts ligated by optically active phosphines, to get atropisomers.[5] Thus, bidentate phosphine ligands that are often optically active[5] were tested.



(27)

From the results collected in Table 6, it is shown that the homocoupling of 1-naphthyl triflate proceeds in the presence of zinc powder as a chemical source of electrons with better yields than in the electrochemical process. This demonstrates that zinc was able to reduce the arylpalladium(II) intermediate.

Various palladium(II) complexes, precursors of palladium(0) catalysts, have been tested. Mixtures of $Pd(OAc)_2$ and phosphines were good catalyst precursors. The mixture $Pd(OAc)_2 + 2PPh_3$ afforded the dimer in a

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(31) (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432. (b) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158. (c) Cabri, W.; De Bernardinis, S.; Francalanci, F.; Penco, S. Santi, R. *J. Org. Chem.* **1990**, *55*, 350. (d) Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T.; Nishioka, E.; Yanagi, K.; Moriguchi, K.-I, *Organometallics* **1993**, *12*, 4188.

(32) In the $NiCl_2(dppe)$-catalyzed electrodimerization of PhBr, the reductive elimination from the complex $Ph_2Ni^{III}Br(dppe)$ was found to be the rate-determining step of the catalytic cycle when the PhBr concentration was high.[13d]

Table 6. Synthesis of 1,1′-Binaphthyl from 1-Naphthyl-OTf Catalyzed by Palladium Complexes, in the Presence of Zinc Powder (Eq 27)[a]

entry	catalyst (10%)	*t*, h	ArAr,[b] %	ArH,[b] %
1	$PdCl_2(PPh_3)_2$	6	59	14
2	$PdCl_2(PPh_3)_2$ + 40LiCl[c]	6	23	13
3	$PdCl_2$(dppf)	6	61	9
4	$Pd(OAc)_2$ + $2PPh_3$	2.5	51	33
5	$Pd(OAc)_2$ + $3PPh_3$	7	67	13
6	$Pd(OAc)_2$ + 1dppe	8	58	31
7	$Pd(OAc)_2$ + 2dppe	8	0	0
8	$Pd(OAc)_2$ + 1dppf	6	64	19
9	$Pd(OAc)_2$ + 1DIOP	7	13	13
10	$Pd(OAc)_2$ + 1BINAP	2.5	98	2
11	$Pd(OAc)_2$ + 2BINAP	2.5	61	39

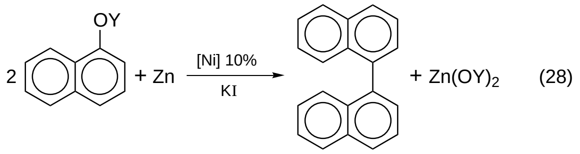
[a] 1-Naphthyl-OTf: 3 mmol in 2 mL of DMF at 90 °C. Zn: 60 mmol. [b] Yields are relative to 1-naphthyl-OTf. [c] Recovered 1-naphthyl-OTf: 32%; 1-naphthol: 26%.

faster reaction but with a smaller yield than the mixture $Pd(OAc)_2$ + $3PPh_3$ (Table 6, entries 4 and 5). It is reported that triphenylphosphine reduces $Pd(OAc)_2(PPh_3)_2$ to a palladium(0) complex and is oxidized to triphenylphosphine oxide.[29b,33] In the present case, zinc powder seems to be a better reductant of the palladium(II) complex than PPh_3. Indeed were the phosphine the reductant, 1 equiv of PPh_3 should be oxidized to triphenylphosphine oxide; therefore, the mixture of $Pd(OAc)_2$ + $2PPh_3$ should produce a palladium(0) complex, not very stable, because it is ligated by only 1 phosphine and therefore not efficient for the coupling. Since the reverse was observed, we are inclined to conclude that zinc powder reduced the mixture $Pd(OAc)_2$ + $2PPh_3$, yielding a palladium(0) complex ligated by $2PPh_3$ that was therefore more reactive than the palladium(0) ligated by $3PPh_3$, produced by reduction of $Pd(OAc)_2$ + $3PPh_3$ by zinc, but also less stable; that is why the yield in dimer is lower (Table 6, entry 4). In those cases, the arylpalladium(II) intermediate is $ArPd(OAc)(PPh_3)_2$. Indeed, in an independent experiment, we established that addition of PhOTf to the palladium(0) generated from the mixture $Pd(OAc)_2$ + 3 PPh_3 led to the formation of $ArPd(OAc)(PPh_3)_2$ by comparison with an authentic sample.[33b]

The fact that a mixture of $Pd(OAc)_2$ + 2dppe gave rise to an inefficient catalyst (probably $Pd(0)(dppe)_2$[34]) also seems to prove that zinc was a better reductant for the palladium(II) complex than dppe (Table 6, entries 6 and 7). Similarly, we think that zinc was a better reductant for the palladium(II) than BINAP[35a] since the dimer was formed in almost quantitative yield (Table 6, entry 10) from the mixture $Pd(OAc)_2$ + 1BINAP.[35b] Under such conditions, the reduction of $Pd(OAc)_2$ + 2BINAP led to $Pd(0)(BINAP)_2$ that was, as expected, less efficient than Pd(0)(BINAP) but still catalyzed the homocoupling (compare Table 6, entries 10 and 11)[35c] contrary to $Pd(0)(dppe)_2$. Among the bidentate ligands tested, BINAP was the most efficient one, affording the fastest homocoupling with quantitative yield in dimer (Table 6, entry 10), which is of interest since this ligand is optically active.

Whereas addition of a large excess of chloride ions generally has a beneficial influence on palladium-catalyzed cross-coupling reactions of aryl triflates with nucleophiles,[14a,b,j,o] in our case, addition of chlorides (Table 6, entry 2) slowed down the reaction and resulted in a poor selectivity (formation of 1-naphthol). In the presence of a large excess of chloride, a new complex was formed $Pd^0(PPh_3)_2Cl_2^{2-}$ known to be less reactive in oxidative additions[22] than $Pd^0(PPh_3)_2Cl^-$, and consequently the direct reduction of 1-naphthyl triflate to 1-naphthol became a competitive process.

Since nickel(0) complexes are able to activate the C−O bond of aryl triflates,[14 l,q] a series of nickel complexes were also tested as catalysts for the dimerization of 1-naphthyl triflate. By comparing Table 6 and Table 7, one observes that nickel complexes were more efficient in the chemical process than palladium complexes, since the homocoupling of the 1-naphthyl triflate was performed at lower temperatures, in a mixture of THF and DMF, with higher yields of dimer.



(28)

We found that $NiCl_2(PPh_3)_2$ was an efficient catalyst when used alone without an excess of ligand.[36] Whereas nickel complexes ligated by bidentate ligands were reported to be inefficient for the dimerization of aryl halides,[12b] we discovered that they were very efficient for the dimerization of aryl triflates, and an almost quantitative yield (93%, Table 7, entry 8) was obtained with $NiCl_2$(dppf) as catalyst. Whereas extra chloride had an inhibited effect on the palladium-catalyzed homocoupling of aryl triflates (see above), on the contrary, the nickel-catalyzed homocoupling needed to be performed in the presence of a large excess of iodide ions, and a decay of the amount of potassium iodide caused a dramatic decay of the yield (Table 7, entries 4 and 7). A large excess of zinc powder was required, and by comparing entries 4−6 (Table 7), we observed that a decrease of the amount of zinc powder resulted in a slower and slower reaction, suggesting that the zinc powder was involved in the rate-determining step of the catalytic cycle. Similar observations were reported for the nickel-catalyzed homocoupling of aryl halides.[12b] A mechanism was proposed in which the monoelectronic reduction of the intermediate $ArNi^{II}XL_2$ complex by zinc was the rate-determining step of the overall process. Addition of iodides would favor the reduction process by formation of a pentacoordinated species $ArNi^{II}XIL_2^-$. In addition to these observations, we propose that iodide ions play a second role. By stabilizing the nickel(0) species, they slow down its oxidative addition with the aryl triflates, avoiding the accumulation (and probably the deactivation) of the arylnickel(II) intermediate, whose reduction by zinc powder is very slow. On the basis of the reported

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(33) (a) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009. (b) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A.; Meyer, G. *Organometallics* **1995**, *14*, 5605.

(34) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1994**, *28*, 287.

(35) (a) It has been reported that mixture of $Pd(OAc)_2$ and 3BINAP resulted in the spontaneous formation of $Pd(0)(BINAP)_2$, 1BINAP was able to reduce the palladium(II) to palladium(0) and was oxidized to BINAP oxide: BINAP(O). See: Osawa, F.; Kubo, A.; Hayashi, T. *Chem. Lett.* **1992**, 2177. (b) Were zinc a poor reductant for the mixture of $Pd(OAc)_2$ and 1BINAP, this system should spontaneously afford BINAP(O) and a poorly reactive naked palladium(0) complex. Since we get the dimer with a good yield, we assume that zinc is a better reductant than binap and that the reduction results in the formation of the very reactive 14e complex: Pd(0)(BINAP). (c) The complex $Pd(0)(BINAP)_2$, although formally an 18e complex, is still able to catalyze Heck reaction. See ref 31d.

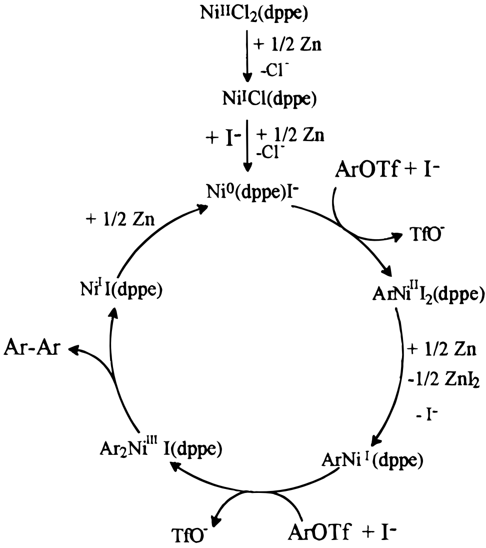
(36) This contrasts with a precedent reported paper.[18a,b]

Table 7. Synthesis of 1,1′-Binaphthyl from 1-Naphthol Derivatives, Catalyzed by Nickel Complexes, in the Presence of Zinc Powder (Eq 28)

n	1-naphthyl-OY,[a] OY	catalyst (10%)	Zn[b]	KI[b]	T, °C	*t*, h	solvent	ArAr,[c] %[c]	ArH,[c] %
1	OTf	$NiCl_2(PPh_3)_2$	20	4	67	4	THF	92	8
2		$NiCl_2$(dppe)	20	4	67	4	THF	60	40
3		$NiCl_2$(dppe)	20	4	67	4	DMF + THF[d]	85	15
4		$NiCl_2$(dppe)	10	4	67	4	DMF + THF[d]	85	14
5		$NiCl_2$(dppe)	7.5	4	67	6	DMF + THF[d]	61	16[e]
6		$NiCl_2$(dppe)	5	4	67	6	DMF + THF[d]	23	9[f]
7		$NiCl_2$(dppe)	10	2	67	4	DMF + THF[d]	3	11
8		$NiCl_2$(dppf)	20	4	67	3.5	DMF + THF[d]	93	6
9	OTs	$NiCl_2(PPh_3)_2$	20	4	140	4	DMF	70	9
10		$NiCl_2$(dppe)	20	4	140	6	DMF	88	10
11	OSO_2PhF[g]	$NiCl_2$(dppe)	20	4	150	6	DMF	45	23
12	$OCONEt_2$	$NiCl_2$(dppe)	20	4	140	16	DMF	0	0[h]
13		$Ni(Acac)_2$	20	4	140	8	DMF	0	0[h]

[a] ArOY: 3 mmol in 2 mL of solvent. [b] Equivalent relative to 1-naphthyl-OY. [c] Yields are relative to 1-naphthyl-OY. [d] DMF + THF (1 mL + 1 mL). [e] Recovered 1-naphthyl-OTf: 12%. [f] Recovered 1-naphthyl-OTf : 69%. [g] *Para* isomer. [h] Recovered 1-naphthyl-OCb: 100%.

Scheme 3



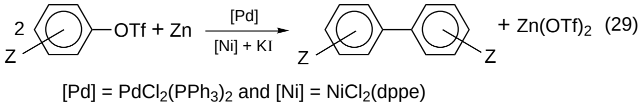
mechanism of the nickel dimerization of aryl halides[12b,13d] and on our own observations, we proposed Scheme 3 for the nickel dimerization of aryl triflates with zinc as electron supplier.

Since nickel complexes are efficient catalysts, the expected less reactive 1-naphthol derivatives were submitted to the homocoupling (Table 7, entries 9−13). The dimer was produced in high yield from the tosylate derivative provided working in pure DMF at higher temperature. The carbamate derivative was totally unreactive even with $Ni(Acac)_2$, yet reported to be efficient in cross-coupling reactions of aryl carbamates with nucleophiles.[14] [1,q] For $NiCl_2$(dppe) as a catalyst, the following order of reactivity was established:

$$ArOSO_2CF_3 > ArOSO_2C_6H_4CH_3 > ArOSO_2C_6H_4F \gg ArOCONEt_2$$

The $NiCl_2(PPh_3)_2$-catalyzed dimerization of aryl mesylates, $ArOSO_2CH_3$, was recently reported,[37] and they were found to be less reactive than aryl triflates.

Thus, the dimerization of 1-naphthyl triflate in the presence of zinc powder has been optimized with two catalysts associated with bidentate ligands, $NiCl_2$(dppf) and $Pd(OAc)_2$ + 1BINAP, opening the way toward optically active ligands. However, before the scope and limitation of the homocoupling of hindered naphthyl and aryl triflates can be defined, the generality of the homocoupling of aryl triflates was investigated with two cheaper catalysts: $NiCl_2$(dppe) and $PdCl_2(PPh_3)_2$ (eq 29).



[Pd] = $PdCl_2(PPh_3)_2$ and [Ni] = $NiCl_2$(dppe)

From the results gathered in Table 8, it is shown that the dimerization of substituted aryl triflates was achieved in good yields with either $PdCl_2(PPh_3)_2$ or $NiCl_2$(dppe) as catalysts that possessed complementary properties.

Indeed, the nickel catalyst was more efficient for the dimerization of aryl triflates substituted by electron-donor groups, while the palladium was found to be more suitable for the dimerization of aryl triflates substituted by electron-withdrawing groups. The nickel(0) complex generated by reduction of $NiCl_2$(dppe) by zinc was so reactive that C−Cl and C−CN bonds were activated, resulting in the formation of byproducts in particular oligomers (Table 8, entries 2 and 8). The palladium(0) complex generated by reduction of $PdCl_2(PPh_3)_2$ by zinc was less reactive, resulting in a good compatibility with functional groups such as CN and Cl. But the palladium(0) could not catalyze the dimerization of unactivated aryl triflates such as those substituted by electron-donor groups. We have already reported that the oxidative addition of palladium(0) complexes with aryl triflates was accelerated by the presence of electron-withdrawing groups (Hammett correlation with $\rho = +2.55$).[15] In the case of poorly reactive aryl triflates, nickel complexes were found to be efficient provided the amount of KI was increased (Table 8, entry 17) or more reactive catalyst such as the one ligated by dppf was used (Table 8, entry 18). In all cases, the homocoupling was regiospecific.

Comparison between the Electrochemical and the Chemical Process. The palladium-catalyzed electrodimerization of aryl triflates (Scheme 1) and the nickel catalyzed dimerization of aryl triflates in the presence of zinc as a chemical reductant (Scheme 3) both proceed by a similar route in the very first steps of the catalytic cycle: formation of an arylpalladium(II) or arylnickel(II) complex that requires further activation by transfer of electrons, supplied by either a cathode or zinc powder.

In the case of the palladium-catalyzed dimerization of very reactive aryl triflates such as those substituted by

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[37] Percec, V.; Bae, J. Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 176.

Table 8. $PdCl_2(PPh_3)_2$- and $NiCl_2$(dppe)-Catalyzed Synthesis of Biaryls from Aryl Triflates in the Presence of Zinc Powder (Eq 29)

n	ZC_6H_4OTf,[a] Z	catalyst[b] (10%)	solvent[c]	*t*, h	*T*, °C	4,4′-Z$(C_6H_4)_2$Z,[d] % (isolated)	ArOTf recovered
1	*p*-CN	Pd	DMF	4	90	(85)	0
2		Ni	DMF + THF	4	67	70 (45)	0[e]
3	*p*-CF_3	Pd	DMF	4	90	(76)	0
4		Ni	DMF + THF	4	67	(93)	0
5	*p*-CO_2Et	Pd	DMF	4	90	69	0
6		Ni	DMF + THF	4	67	86 (63)	0
7	*p*-Cl	Pd	DMF	5	90	17	47
8		Ni	DMF + THF	4	67	0	0[f]
9	*p*-F	Ni	DMF + THF	4	67	(85)	0
10	H	Pd	DMF	4	90	30	32
11		Ni	DMF + THF	4	67	(99)	0
12	*p*-Me	Pd	DMF	4	90	7	66
13		Ni	DMF	6	90	(94)	0
14	*o*-Me	Pd	DMF	6	90	0	100
15		Ni	DMF	6	90	(53)[g]	0
16	*p*-MeO	Pd	DMF	4	90	0	100
17		Ni[h]	DMF + THF	4	67	(98)	0
18	*p*-*t*-Bu	Ni[i]	DMF	6	90	(36)	55

[a] ZC_6H_4OTf: 3 mmol; Zn: 60 mmol. [b] Pd = $PdCl_2(PPh_3)_2$: 0.3 mmol; Ni = $NiCl_2$(dppe): 0.3 mmol + KI (12 mmol). [c] The reactions were performed in 2 mL of DMF or in a mixture of 1 mL of DMF and 1 mL of THF. [d] Yields are based on the initial aryl triflate and were determined on the crude mixture, after workup, by ^1H NMR spectroscopy using $CHCl_2CHCl_2$ as internal standard. [e] Formation of 4,4″-CN$(C_6H_4)_3$CN. [f] Formation of 42% (isolated yield) of 4,4‴-Cl$(C_6H_4)_4$Cl. [g] 2,2′-Me$(C_6H_4)_2$Me. [h] 18 mmol of KI. [i] $NiCl_2$(dppf).

Table 9: Comparison between the Electrochemical and the Chemical Process

	ArOTf, Ar	catalyst (10%)	electron source	*t*,[a] h	*T*, °C	ArAr, %
1	*p*-$CF_3C_6H_4$−	$PdCl_2(PPh_3)_2$	cathode	4	90	68
2	*p*-$CF_3C_6H_4$−	$PdCl_2(PPh_3)_2$	Zn	4	90	76
3	C_6H_5−	$PdCl_2(PPh_3)_2$	cathode	4	90	83
4	C_6H_5−	$PdCl_2(PPh_3)_2$	Zn	4	90	30
5	C_6H_5−	$NiCl_2$(dppe)[b]	Zn	4	67	99
6	*p*-$MeOC_6H_4$−	$PdCl_2(PPh_3)_2$	cathode	4	90	15
7	*p*-$MeOC_6H_4$−	$PdCl_2(PPh_3)_2$	Zn	4	90	0
8	*p*-$MeOC_6H_4$−	$NiCl_2$(dppe)[b]	Zn	4	67	98
9	1-naphthyl−	$PdCl_2(PPh_3)_2$	cathode	4	90	51
10	1-naphthyl−	$PdCl_2(PPh_3)_2$	Zn	6	90	59
11	1-naphthyl−	$NiCl_2$(dppe)[c]	cathode	3	90	56
12	1-naphthyl−	$NiCl_2$(dppe)[b]	Zn	4	67	82

[a] Reaction times. [b] In the presence of 4 equiv of KI compared to the aryl triflate. [c] The electrosynthesis was performed in DMF at −1.7 V *vs* SCE.

electron-withdrawing groups (see, for example, entries 1 and 2 of Table 9), the efficiency of the electrochemical and the chemical processes was comparable.

More interesting is the comparison of the two processes for the dimerization of less reactive aryl triflates. Indeed, the palladium-catalyzed dimerization of C_6H_5OTf and *p*-$MeOC_6H_4OTf$ was found to be more efficient when performed electrochemically (compare Table 9, entries 3 and 4, 6 and 7). This is easily interpreted by the fact that the intermediate arylpalladium(II) complexes, when substituted by electron-donor groups, are reduced at very negative potentials (see Table 1). In such cases, the zinc powder was not able to reduce them, and thus, the reaction was limited by the reducing power of the chemical reductant, whereas very high negative potentials were easily reached by simply tuning the potential of the cathode. However, by changing the catalyst from $PdCl_2(PPh_3)_2$ to $NiCl_2$(dppe), the chemical reduction by zinc became more efficient than the electrochemical process (compare Table 9, entries 3−5, 6−8). Arylnickel(II) complexes are more easily reduced than the corresponding arylpalladium(II) complexes and therefore are easily reduced by zinc (*e.g.*, the reduction peak potential of PhNiCl(dppe) is −1.80 V *vs* SCE[13d] whereas that of $PhPdCl(PPh_3)_2$ is −2.20 V[26]). It should also be mentioned that the nickel-catalyzed chemical dimerization was achieved at lower temperatures because oxidative additions of nickel(0) complexes are always faster than that performed from palladium(0) complexes. The palladium-catalyzed chemical or electrochemical homocoupling of 1-naphthyl triflate afforded comparable yields (Table 9, entries 9 and 10). When performed with a nickel catalyst, the chemical process was more efficient than the electrochemical one, but the former should be carried out in the presence of potassium iodide. This means that the reductant power of the zinc powder was too low to reduce the corresponding ArNiCl(dppe) complex, which is formed in the absence of iodides, but that it was high enough to reduce an $ArNiI_2(dppe)^-$, complex formed when the oxidative addition was performed in the presence of iodide ions (Scheme 3).

Palladium- or Nickel-Catalyzed Homocoupling of Hindered Aryl Triflates in the Presence of Zinc Powder. When substituted in the *ortho* and *ortho′* positions, biaryls become optically active, and these atropisomers may be used as optically active ligands[5] or be their precursors. Our purpose was to extend the catalytic homocoupling of aryl triflates described above to the synthesis of atropisomers and to use optically active ligands on the metal in order to perform asymmetric homocoupling. Indeed, to our knowledge, no example of catalytic asymmetric homocoupling of aryl triflates (or halides) has been reported.[38] Since the dimerization of 1-naphthyl triflate was found to be quantitative with $Pd(OAc)_2$ + 1BINAP or $NiCl_2$(dppf) as catalysts, the latter were tested in the homocoupling of hindered aryl triflates (although dppf is not an optically active ligand, it was, however, tested as a model since some optically active ligands derive from substituted ferrocene[5b,39]). The dimerization of compound **1**, in which the 1-naphthyl triflate was substituted by a methyl group, in the *ortho* position, was achieved using $NiCl_2$(dppf) as catalyst (Table 10).

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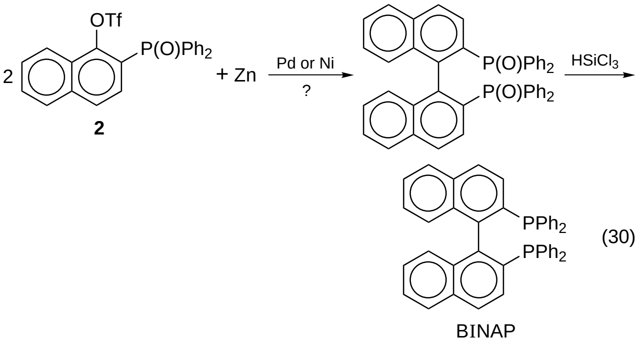
(38) Racemic diphosphines in the biphenyls series were synthesized from aryl iodides by an Ullmann reaction in the presence of a stoechiometric amount of copper(0). See: Schmid, R.; Foricher, J.; Cereghetti, M.; Schönholzer, P. *Helv. Chim. Acta* **1991**, *74*, 370.

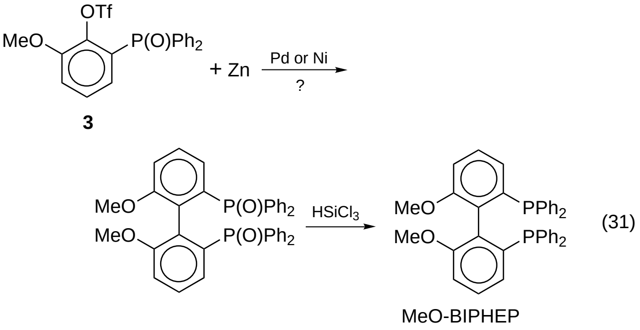
(39) Zhang, W.; Hirao, T.; Ikeda, I. *Tetrahedon Lett.* **1996**, *37*, 4545.

Surprisingly, the homocoupling did not work in the presence of an optically active ligand such as (*S*,*R*)-PPFOMe associated to $NiBr_2$ (the arene was only formed in 85% yield), although this ligand was very efficient in the enantioselective cross-coupling reaction between 2-methyl-1-naphthyl bromide and (2-methyl-1-naphthyl)-magnesium bromide.[5b] This suggests that the intermediates of the homocoupling and the cross-coupling are different (see Scheme 3). The palladium(0) complex generated from the mixture of $Pd(OAc)_2$ + 1(*S*)-BINAP catalyzed the homocoupling but with a very low yield compared to that of the reported cross-coupling reaction,[5b] so no effort was undertaken to determine whether the resulting dimer was optically active or not. Nevertheless, the homocoupling of hindered aryl triflates seemed to be feasible, even from an aryl triflate deactivated in the oxidative additions by the presence of the methyl group as electron donor, in the *ortho* position.

Therefore, two unreported *ortho*-substituted aryl triflates, compounds **2** and **3**, were synthesized in four steps according to Schemes 4 and 5, with an overall yield of 56% and 49%, respectively.

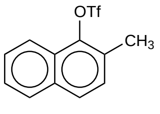
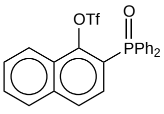
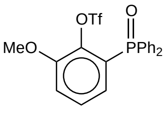
The homocoupling of compound **2** should produce the diphosphine dioxide, a precursor[40] of the BINAP ligand[5c−h] (eq 30), whereas that of compound **3** should produce the corresponding dimer, a precursor[40] of the MeO-BIPHEP ligand[5k−m] (eq 31).





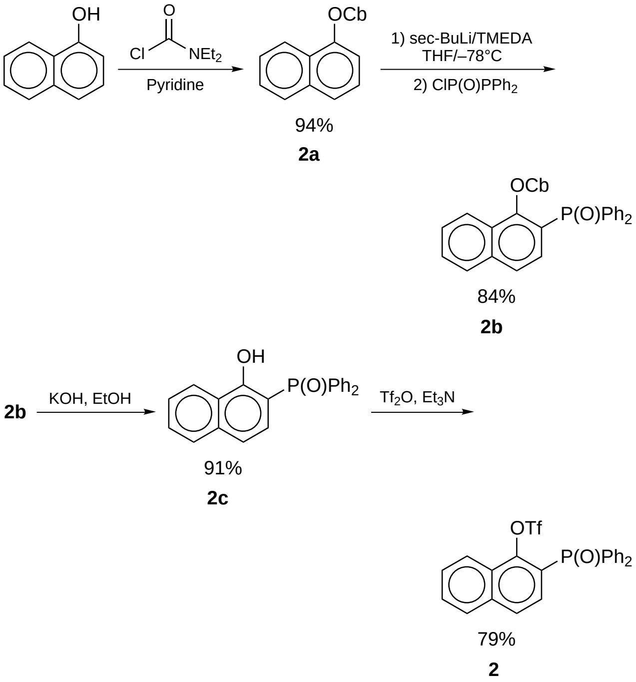
P(O)Ph_2 was chosen as a substituent in the *ortho* position rather than PPh_2 because it is an electron-withdrawing group that should accelerate the rate of the oxidative additions and the resulting dimer (phosphine oxide) should not be a good ligand for palladium or nickel complexes compared to the corresponding diphosphine.[41]

Table 10. Palladium or Nickel Catalyzed Dimerization of Hindered Aryl Triflates in the Presence of Zinc Powder

ArOTf[a]	catalyst, (10%)	*t*, h	ArAr, %	ArH, %
 **1**	$NiCl_2$(dppf)[b] $Pd(OAc)_2$ + 1(*S*)-BINAP	2 7	66 16	19 60
 **2**	$NiCl_2$(dppf)[b] $Pd(OAc)_2$ + 1(*S*)-BINAP	1 2	0 0	93 88
 **3**	$NiCl_2$(dppf)[b] $Pd(OAc)_2$ + 1(*S*)-BINAP	18 18	0 0	24[c] 23[d]

[a] The reactions were performed at 100 °C. **1**/Zn: 0.5 mmol/10 mmol in 0.5 mL of DMF. **2**/Zn: 0.2 mmol/4 mmol in 0.2 mL of DMF. **3**/Zn: 0.2 mmol/4 mmol in 0.2 mL of DMF. [b] In the presence of 4 equiv of KI relative to the aryl triflate. [c] Formation of ArOH (15%). Recovered ArOTf (40%). [d] Formation of ArOH (20%). Recovered ArOTf (37%).

Scheme 4



However, neither $NiCl_2$(dppf) nor $Pd(OAc)_2$ + 1(*S*)-BINAP catalyzed the homocoupling of compound **2**; the corresponding arene was only formed by a fast reaction (Table 10). These results suggest that, whatever the catalyst, the first oxidative addition of the palladium(0) (or nickel(0)) proceeds well (Schemes 2 and 3) leading to the corresponding arylpalladium(II) (or arylnickel(II)) complex but that the activation of these intermediates by electron transfer produced a complex unable to undergo a second oxidative addition with the aryl triflate, probably due to steric hindrance around the metal. A similar behavior was observed for compound **3**, except that the formation of the arene was slower probably due to the deactivating effect of the methoxy group, an

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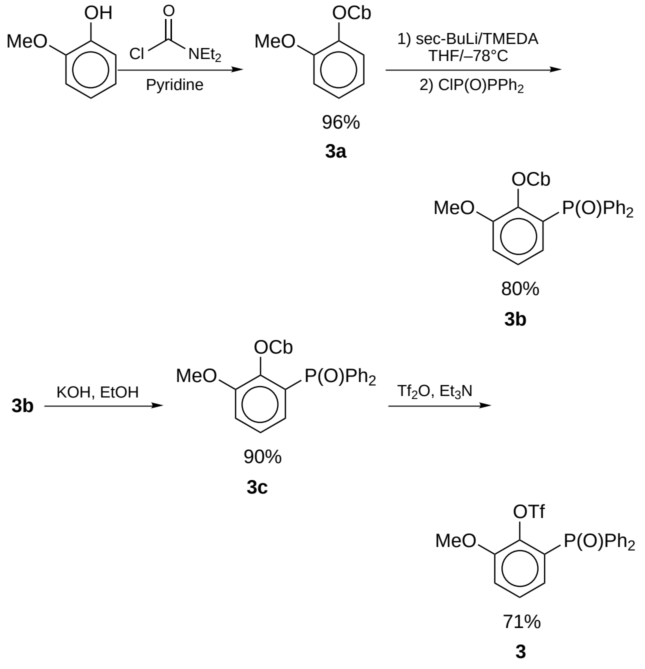
(40) For the reduction of phosphine oxide to the corresponding phosphine see: (a) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012. (b) Uozomi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945.

(41) Indeed, we observed from Table 6 that using two bidentate phosphine ligands per palladium resulted in either a nonreactive catalyst (entry 7) or a less efficient one (entry 11).

Scheme 5



electron donor, in the oxidative addition. Therefore, steric hindrance appears to be a severe limitation for the palladium- or nickel-catalyzed homocoupling of aryl triflates.

Conclusion

It is shown that phenols, which are commonly available compounds, are converted to the corresponding biaryls *via* the triflate derivatives, in the presence of a catalytic amount of a palladium or a nickel complex and an electron source, either a cathode or zinc powder. Best

$$\mathrm{ArOH} \xrightarrow{(\mathrm{Tf})_2\mathrm{O}} \mathrm{ArOTf} \xrightarrow{+\mathrm{e},\ [\mathrm{Pd}]\ \mathrm{or}\ [\mathrm{Ni}]} \mathrm{ArAr}$$

yields in the binaphthyl series were obtained with nickel and palladium complexes, when ligated by bidentate ligands, such as dppf and BINAP, respectively. The homocoupling proceeds by activation of the C−O bond of the aryl triflate by a palladium(0) or a nickel(0) complex, affording an arylpalladium(II) or nickel(II) complex whose activation by electron transfer produces a new complex able to undergo a second oxidative addition with the aryl triflate followed by formation of the dimer. Whereas aryl triflates are usually known to react with nucleophiles in the presence of a palladium or a nickel catalyst, electron transfer results in an inversion of their reactivity since it was shown in this work that they react with themselves, which means with electrophiles.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 200 MHz or at 250 MHz (TMS as internal reference). ^{31}P NMR spectra were recorded at 101.2 MHz (H_3PO_4 as external reference). ^{13}C and ^{19}F NMR spectra were recorded at 62.9 (TMS as internal reference) and at 235 MHz ($CFCl_3$ as external reference), respectively.

All reactions were performed under argon in vessel connected to a Schlenk line. Flash chromatography was performed with silica gel 60, 230−400 mesh (Merck).

Chemicals. Tetrahydrofuran was distilled on sodium/benzophenone and dimethylformamide on calcium hydride under reduced pressure. The solvents were degassed prior use. Zinc powder (200 mesh) was commercial (Acros Organics). (*S*)-BINAP, (S,*R*)-PPFOMe, DIOP, and dppf were commercial (Aldrich). $PdCl_2(PPh_3)_2$,[42] $PdCl_2(MePPh_2)_2$,[42] $PdCl_2$(dppm),[31a] $PdCl_2$(dppe),[43] $PdCl_2$(dppp),[31a] $PdCl_2$(dppb),[31a] $PdCl_2$(dppf),[31b] $NiCl_2$(dppe),[44] and $NiCl_2$(dppf)[44] were synthesized according to reported procedures. 1-Naphthyl triflate,[45] and 2-methyl-1-naphthyl triflate (**1**) were synthesized from 1-naphthol and 2-methyl-1-naphthol (commercial from Aldrich), respectively, by reaction of the naphthol with trifluoromethanesulfonyl anhydride in the presence of triethylamine in dichloromethane. *Para*- and *ortho*-substituted phenyl triflates were synthesized from the corresponding phenols (commercial from Aldrich) according to the same procedure.[45] They were characterized by their ^{1}H NMR and mass spectra, which were identical to those of previously reported compounds.[14a,19]

2-Methyl-1-naphthyl triflate (1): 10.1 g (92% yield); oily liquid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.65−7.48 (m, 2H), 7.36 (d, $J = 8.5$ Hz, 1H), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 142.8 (−*C*O), 133.5, 128.9, 128.4, 128.2, 127.8, 127.6, 127.1, 126.3, 120.9, 118.7 (q, $J_{CF} = 320$ Hz, CF_3), 17.2 (CH_3); *m/e* (CI NH_3) 308 (M + 18), 290 (M^+). Anal. Calcd for $C_{12}H_9F_3O_3S$: C, 49.66; H, 3.13. Found: C, 49.74, H: 3.12.

1-Naphthyl tosylate was synthesized using a procedure similar to the synthesis of 1-naphthyl triflate.[45] To a stirred solution of 1-naphthol (4.32 g, 30 mmol) in 170 mL of distilled dichloromethane and triethylamine (4.87 mL, 35 mmol) at −50 °C was added dropwise *p*-toluenesulfonyl chloride (6.67 g, 35 mmol) for 10 min. After being warmed overnight to room temperature, the solution was hydrolyzed with aqueous HCl (10%). The organic phase was washed with water and dried over $MgSO_4$. After evaporation of the solvent, the crude mixture was crystallized from dichloromethane and petroleum ether: white crystals; 7.6 g (85% yield); mp = 92 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.93 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.84−7.73 (m, 2H), 7.79 (d, $J = 8$ Hz, 2H), 7.52−7.43 (m, 2H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.28 (d, $J = 8$ Hz, 2H), 7.21 (dd, $J = 7.5$, 1.5 Hz, 1H), 2.42 (s, 3H); *m/e* (EI) 298 (M^+), 155, 143, 115, 91.

1-Naphthyl *p*-Fluorobenzenesulfonate. Same procedure as for the synthesis of 1-naphthyl tosylate, from 1-naphthol (4.32 g, 30 mmol) and *p*-fluorobenzenesulfonyl chloride (6.81 g, 35 mmol), was used: white crystals; 8.5 g (94% yield); mp = 93 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.91 (dd, $J = 8.5$ Hz, $J = 5$ Hz, 2H), 7.86−7.82 (m, 2H), 7.78 (d, $J = 8$ Hz, 1H), 7.52−7.44 (m, 2H), 7.39 (t, $J = 8$ Hz, 2H), 7.17 (t, $J = 8.5$ Hz, 2H); *m/e* (EI) 302 (M^+), 143, 115 (100), 95.

1-Naphthyl *N,N*-Diethylcarbamate (2a).[46] To a stirred solution of 1-naphthol (7.2 g, 50 mmol) in 250 mL of anhydrous pyridine was slowly added *N,N*-diethylcarbamoyl chloride (6.77 g, 50 mmol). The solution was stirred under reflux for 6 h and then poured over ice and extracted with ethyl ether. The organic phase was washed with aqueous HCl 10% and then with a $NaHCO_3$ aqueous solution and dried on $MgSO_4$. After flash chromatography, 11.42 g of pure **2a** was collected as pale orange crystals (94% yield): mp = 120 °C; ^{1}H NMR (250 MHz $CDCl_3$) δ 7.96−7.86 (m, 2H), 7.72 (d, $J = 8$ Hz, 1H), 7.55−7.49 (m, 2H), 7.46 (d, $J = 8$ Hz, 1H), 7.31 (d, $J = 7$ Hz, 1H), (q, $J = 7$ Hz, 2H), 3.47 (q, $J = 7$ Hz, 2H), 1.40 (t, $J = 7$ Hz, 3H), 1.27 (t, $J = 7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 154.2 (s, *C*=O), 147.4 (s, *C*O), 134.6 (s), 127.9 (d), 127.5 (s), 126.1 (d), 125.4 (d), 125.2 (d), 121.2 (d), 118 (d), 42.3 (t, CH_2), 42 (t, CH_2), 14.4 (q, CH_3), 13.4 (q, CH_3); IR (KBr pellet) 1730 ($\nu_{C=O}$) cm^{-1}; *m/e* (CI NH_3) 261 (M + 18), 244 (M + 1).

2-(Diphenylphosphinyl)-1-naphthyl *N,N*-diethylcarbamate (2b) was synthesized according to the procedure reported for the *ortho* lithiation of *O*-aryl carbamates.[47] A solution of *s*-BuLi (35 mL of a solution 1.4 M, 48 mmol) was

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added to 70 mL of THF at −78 °C, followed by TMEDA (7.25 mL, 48 mmol). A solution of 1-naphthyl *N*,*N*-diethylcarbamate (9.72 g, 40 mmol) in 50 mL of THF was added. After 45 min, the anion was quenched with $ClP(O)Ph_2$ (9.2 mL, 48 mmol) at −78 °C. After being warmed overnight to room temperature, the solution was hydrolyzed with water and extracted with diethyl ether. Flash chromatography performed on the crude mixture (eluent: petroleum ether/ethylacetate, 8/2) afforded 14.9 g of **2b** as white crystals (84% yield): mp = 121 °C; ^1H NMR (250 MHz $CDCl_3$) δ 7.87 (d, J = 8 Hz, 1H), 7.81−7.67 (m, 6H), 7.58−7.46 (m, 8H), 7.31 (dd, J = 12, 8 Hz, 1H), 3.50−3.39 (m, 1H), 3.17−3.06 (m, 2H), 2.98−2.90 (m, 1H), 1.16 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 152.4, 151.8, 136.6, 133.6 (d, J = 80 Hz), 132.0, 131.9, 131.8 (d, J = 6.5 Hz), 128.4, 128.1 (d, J = 16 Hz), 127.8, 127.0, 125.5 (d, J = 11 Hz), 122.8, 122.4 (d, J = 102 Hz), 42.2, 41.8, 14.2, 13.1; ^{31}P NMR ($CDCl_3$) δ 27.45; IR (KBr pellet) 1731 ($\nu_{C=O}$), 1272 ($\nu_{P=O}$) cm^{-1}; *m*/*e* (EI) 443 (100, M^+), 344, 219, 201, 100.

2-(Diphenylphosphinyl)-1-naphthol (2c). 2-(Diphenylphosphinyl)-1-naphthyl *N*,*N*-diethylcarbamate (13.3 g, 30 mmol) and potassium hydroxide (8 g, 140 mmol) were stirred in 200 mL of ethanol under reflux for 16 h.[48] The solution was neutralized with HCl (10%) and extracted with dichloromethane. The crude product was purified by chromatography (eluent: petroleum ether/ethyl acetate, 7/3) followed by crystallization from dichloromethane−petroleum ether, which yields **2c**, 9.35 g (91%), as pink crystals: mp = 170 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 12.3 (s, 1H, OH), 8.42 (dd, J = 8.5, 1.7 Hz, 1H), 7.8−7.69 (m, 5H), 7.62−7.44 (m, 8H), 7.27−7.23 (m, 1H), 7.04 (dd, J = 12, 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 162.7 (d, J = 2.7 Hz), 136.4, 132.5 (d, J = 2.7 Hz), 132 (d, J = 10.5 Hz), 131.9 (d, J = 105 Hz), 128.9, 128.6 (d, J = 12.5 Hz), 127.3, 126 (d, J = 10.5 Hz), 125.9, 125.7 (d, J = 9 Hz), 123.3, 118.8 (d, J = 12 Hz), 102.2 (d, J = 106 Hz); ^{31}P NMR ($CDCl_3$) δ 40.6; *m*/*e* (CI NH_3) 345 (M + 1). Anal. Calcd for $C_{22}H_{17}O_2P$: C, 76.74; H, 4.98. Found: C, 76.83; H, 5.04. The spectra were identical to those reported for the same compound prepared according to another procedure.[49]

2-(Diphenylphosphinyl)-1-naphthyl triflate (2). The same procedure as for the synthesis of 1-naphthyl triflate[45] was followed except that a large excess of NEt_3 (4 equiv) and trifluoromethanesulfonic anhydride (4 equiv) relative to **2c** (8.6 g, 25 mmol) was necessary. Flash chromatography over alumina and crystallization from petroleum ether and dichloromethane give 9.25 g of **2** as colorless crystals (78% yield): mp = 170 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.35−8.20 (m, 1H), 7.93−7.88 (m, 1H), 7.78−7.67 (m, 7H), 7.57−7.46 (m, 6H), 7.27 (dd, J = 12, 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 149.2, 136.2 (d, J = 2 Hz), 132.6 (d, J = 108 Hz), 132.0 (d, J = 10 Hz), 129.2, 128.6 (d, J = 12 Hz), 128.2, 127.8, 127.5 (d, J = 11 Hz), 127.0 (d, J = 6 Hz), 123.32 (d, J = 97 Hz), 122.3, 118.7 (q, J_{CF} = 315 Hz, CF_3); ^{31}P NMR ($CDCl_3$) δ 28.20; ^{19}F NMR ($CDCl_3$) δ −72.15; IR (KBr pellet) 3056, 1628, 1592, 1563, 1433, 1216 ($\nu_{P=O}$) cm^{-1}; *m*/*e* (CI NH_3) 477 (M + 1). Anal. Calcd for $C_{23}H_{16}F_3O_4PS$: C, 57.99; H, 3.39. Found: C, 58.17; H, 3.42.

2-Methoxyphenyl *N*,*N*-Diethylcarbamate (3a). The same procedure as for **2a** from 2-methoxyphenol (6.2 g, 50 mmol)was followed. A total of 10.7 g of **3a** was isolated as an orange oil (96% yield): ^1H NMR (200 MHz, $CDCl_3$) δ 7.26−7.06 (m, 2H), 6.96−6.88 (m, 2H), 3.82 (s, 3H), 3.42 (broad q, 4H), 1.23 (broad t, 6H); ^{13}C NMR ($CDCl_3$) δ 154.2 (C=O), 151.6 (CO), 140.6, 126.2, 123.4, 120.7, 112.5, 55.9 (OCH$_3$), 42.3 (CH$_2$), 42.0 (CH$_2$), 14.1 (CH$_3$), 13.5 (q, CH$_3$); *m*/*e* (CI NH_3) 224 (M + 1).

2-(Diphenylphosphinyl)-6-methoxyphenyl *N*,*N*-Diethylcarbamate (3b). The same procedure as for **2b** was followed. The reaction was performed from **3a** (8.9 g, 40 mmol). **3b**: colorless crystals; 13.5 g (80%, yield); mp = 89 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.84−7.63 (m, 4H), 7.60−7.37 (m, 6H), 7.22 (td, J = 7 Hz, J_{PH} = 3.5 Hz, 1H), 7.16 (dd, J = 7, 2 Hz,1H), 7.05 (ddd, J_{PH} = 12.5 Hz, J = 7, 2 Hz,1H), 3.82 (s, 3H), 3.04 (broad q, J = 7 Hz, 2H), 2.91 (broad q, J = 7 Hz, 2H), 1.00 (t, J = 7 Hz, 3H), 0.92 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 152.3, 151.61, 142.9, 131.8 (d, J = 10.5 Hz), 131.6, 128.1 (d, J = 12 Hz), 127.2, 125.8 (d, J = 14 Hz), 125.2 (d, J = 7.5 Hz), 117.0, 56.3 (OCH$_3$), 42.0 (CH$_2$), 41.7 (CH$_2$), 13.7 (CH$_3$), 13.0 (CH$_3$); ^{31}P NMR ($CDCl_3$) δ 26.89; IR (KBr pellet) 1717 ($\nu_{C=O}$), 1214 ($\nu_{P=O}$) cm^{-1}; *m*/*e* (CI NH_3) 424 (M + 1).

2-(Diphenylphosphinyl)-6-methoxyphenol (3c). The Same procedure as for **2c** was followed. The reaction was performed from **3b** (12.7 g, 30 mmol) with a reflux of 24 h. **3c** was isolated as pale pink crystals after chromatography (eluent: petroleum ether/ethylacetate, 7/3): 8.74 g (90% yield); mp = 164 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 11.04 (broad s, 1H, OH), 7.73−7.64 (m, 4H), 7.59−7.52 (m, 2H), 7.49−7.41 (m, 4H), 6.98 (broad d, J = 7.9 Hz, 1H), 6.80 (td, J = 7.9 Hz, J_{PH} = 4.2 Hz, 1H), 6.64 (ddd, J_{PH} = 12.5 Hz, J = 7.9, 1.5 Hz, 1H), 3.87 (s, OCH_3); ^{13}C NMR ($CDCl_3$) δ 153.5, 149.0 (d, J = 11 Hz), 132.6 (d, J = 2.8 Hz), 132.1 (d, J = 10.5 Hz), 131.0, 128.7 (d, J = 12.5 Hz), 123.3 (d, J = 9.5 Hz), 119.2 (d, J = 14.5 Hz), 115.3, 111.7 (d, J = 103 Hz), 56.1 (OCH$_3$); ^{31}P NMR ($CDCl_3$) δ 38.90; *m*/*e* (CI NH_3) 325 (M + 1). Anal. Calcd for $C_{19}H_{17}O_3P$: C, 70.37; H, 5.28. Found: C, 70.28; H, 5.35.

2-(Diphenylphosphinyl)-6-methoxyphenyl Triflate (3). Same procedure as for **2**. The reaction was performed from **3c** (4.9 g, 15 mmol). The crude mixture was chromatographed (eluent: petroleum ether/ethylacetate, 6/4) and afforded 4.8 g of **3** as colorless crystals (71% yield): mp = 164 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.76−7.67 (m, 4H), 7.57−7.44 (m, 6H), 7.33 (td, J = 8 Hz, J_{PH} = 2.5 Hz, 1H), 7.23 (dd, J = 8, 1.5 Hz, 1H) 6.94 (ddd, J_{PH} = 12.5 Hz, J = 8, 1.5 Hz, 1H), 3.90 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 151.3 (d, J = 8.3 Hz), 140.7, 132.3 (d, J = 3 Hz), 132.0 (d, J = 10.1 Hz), 130.6, 128.6 (d, J = 12.6 Hz), 128.2, 127.2, 126 (d, J = 7.7 Hz), 118.7 (q, J_{CF} = 322 Hz, CF$_3$), 117.3 (d, J = 2.2 Hz), 56.1 (OCH$_3$); ^{31}P NMR ($CDCl_3$) δ 26.1; ^{19}F NMR ($CDCl_3$) δ −70.83; IR (KBr pellet) 3055, 2995, 1608, 1570, 1474, 1420, 1430, 1293 (ν_{COMe}), 1210 ($\nu_{P=O}$) cm^{-1}; *m*/*e* (CI NH_3) 457 (M + 1). Anal. Calcd for $C_{20}H_{16}F_3O_5PS$: C, 52.64; H, 3.53. Found: C, 52.74; H, 3.58.

Electrochemical Setup and Electrochemical Procedure for Cyclic Voltammetry. Cyclic voltammetry was performed with a homemade potentiostat[50] and a waveform generator, PAR Model 175. The cyclic voltammograms were recorded with a Nicolet 3091 digital oscilloscope. Experiments were carried out in a three-electrode cell connected to a Schlenk line. The cyclic voltammetry was performed at a stationary disk electrode (a gold disk made from cross section of wire (∅ = 0.5 mm) sealed into glass) with a scan rate of 0.2 V s^{-1} or 0.05 V s^{-1}. The counterelectrode was a platinum wire of *ca.* 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge (3 mL) filled with a 0.3 M *n*-Bu_4NBF_4 solution in DMF. Twelve mL of DMF containing 0.3 M *n*-Bu_4NBF_4 was poured into the cell.

General Procedure for Cyclic Voltammetry. A 16.8 mg amount of $PdCl_2(PPh_3)_2$ (0.024 mmol, 2 mM) was added to the cell and the cyclic voltammetry performed. The 1-naphthyl triflate (0.048 mmol, 4 mM and successively 10 and 20 mM) was then added and cyclic voltammetry performed again. In an other set of experiments corresponding to the experimental conditions of the electrolyses, the cyclic voltammetry was performed just before the electrolysis first on the aryl triflate alone (1 mmol, 20 mM) in 50 mL of DMF and then in the presence of a 70 mg amount of $PdCl_2(PPh_3)_2$ (0.1 mmol, 2 mM).

General Procedure for Preparative Electrolyses. Preparative electrolyses were carried out at room temperature in a two-compartment air-tight three-electrode cell. The two compartments were separated by a sintered glass disk (porosity 4). The cathode was a carbon cloth (*ca.* 10 cm^2 surface area). The anode was a magnesium rod. The reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge (3 mL) filled with a 0.3 M *n*-Bu_4NBF_4 solution in DMF. The cathodic and anodic compartments were filled with 50 and 5 mL, respectively, of DMF containing

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n-Bu_4NBF_4 (0.3 M). One mmol of the aryl triflate was added to the cell followed by 70 mg (0.1 mmol) of $PdCl_2(PPh_3)_2$. The electrolysis was conducted at controlled potential and was stopped when the current was about 5% of its initial value. The cathodic compartment was hydrolyzed with aqueous HCl (1 N) and extracted with diethyl ether. The yields of biaryls, arenes, and ArOH were determined on the crude mixture by ^1H NMR spectroscopy (250 MHz), using $CHCl_2CHCl_2$ as internal standard, and by comparison with the authentic samples, when available. The biaryls were then isolated by flash chromatography (eluent: petroleum ether/ethylacetate) and characterized by NMR and mass spectroscopy.

General Procedure for the Synthesis of Biaryls in the Presence of Zinc Powder. Zinc powder was activated by treatment of 20 g in 100 mL of acetic acid for 1 h. After filtration, the powder was washed three times with distilled water. It was dried under vacuum for 6 h at 120 °C. $NiCl_2$(dppe) (0.158 g, 0.3 mmol), zinc powder (3.9 g, 60 mmol), KI (2 g, 12 mmol), and the aryl triflate (3 mmol) were stirred in 2 mL of degassed solvent (DMF or THF) at the desired temperature. The reaction was monitored by TLC or HPLC. The mixture was hydrolyzed with aqueous HCl 10% and extracted with ethyl ether. The organic phase was washed with water and dried over $MgSO_4$. The crude mixture was treated as described above for the electrosyntheses.

1,1′-Binaphthyl:[51] mp = 144−145 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.945, 7.943 (2d, $J = 8.2$ Hz, 4H), 7.58 (t, $J = 7$ Hz, 2H), 7.50−7.37 (m, 6H), 7.31−7.24 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 138.4, 133.5, 132.8, 128.1, 127.9, 127.8, 126.5, 125.9, 125.7, 125.3; *m/e* (EI) 254 (100 M^+), 253, 252, 239 ,126.

4,4′-Dicyanobiphenyl:[52] mp = 233−234 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.8 (d, $J = 8.6$ Hz, 4H), 7,7 (d, $J = 8.6$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 144 ($-C$CN), 133, 128, 118 ($-C$N), 113; IR (KBr pellet) 3080, 2210 ($\nu_{C\equiv N}$), 1420, 1480, 580 cm^{-1}; *m/e* (EI) 204 (100, M^+), 177.

4,4′-Bis(trifluoromethyl)biphenyl:[53] mp = 92−93 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.78 (d, $J = 8.8$ Hz, 4H), 7.71 (d, $J = 8.8$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 143.2, 130.3 (q, $J_{CF} = 34.5$ Hz, $-CCF_3$), 127.6, 125.8 (q, $J_{CF} = 3.4$ Hz, $-CCCF_3$), 124 (q, $J_{CF} = 272$ Hz, CF_3); *m/e* (EI) 290 (M^+, 100) 271, 221, 152.

4,4′-Dichlorobiphenyl:[54] mp = 147−148 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.49 (d, $J = 8.5$ Hz, 4H), 7,42 (d, $J = 8.5$ Hz, 4H); *m/e* (EI) 224,222 (100, M^+), 188, 190, 152.

2,2′-Dichlorobiphenyl:[55] mp = 59 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.61 (d, $J = 7$ Hz, 2H), 7.46 (td, $J = 7$, 1.5 Hz, 2H), 7.39−7.30 (m, 4H); *m/e* (EI) 224,222 (M^+), 205, 187, 154,152 (100).

Biphenyl:[51] mp = 70 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.67 (dd, $J = 8.8$, 2 Hz, 4H), 7.33 (dd, $J = 8.8$, 7.5 Hz, 4H), 7.33 (dd, $J = 7.5$, 2 Hz, 2H); *m/e* (EI) 154 (100, M^+), 76, 57.

4,4′-Dimethoxybiphenyl:[51] mp = 179 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.49 (d, $J = 8.6$ Hz, 4H), 6.97 (d, $J = 8.6$ Hz, 4H), 3.86 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 158.6 ($COCH_3$), 133.4, 127.7, 114.1, 55.3 (OCH_3); *m/e* (EI) 214 (100, M^+), 199, 171.

2,2′-Bipyridine:[51] mp = 70−71 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 8.68 (dd, $J = 4.8$, 1.6 Hz, 2H), 8.40 (dd, $J = 7.8$, 1 Hz, 2H), 7.82 (td, $J = 7.8$, 1.6 Hz, 2H), 7.31 (ddd, $J = 7.8$, 4.8, 1 Hz, 2H); *m/e* (EI) 156 (M^+).

4,4′-Dicarbethoxybiphenyl:[52] mp = 224−226 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 8.15 (d, $J = 8.4$ Hz, 4H), 7.66 (d, $J = 8.4$ Hz, 2H), 4.43 (q, $J = 7.1$ Hz, 4H), 1.44 (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 166.3 ($C{=}O$), 144.2 ($CC{=}O$), 130.1, 123.0, 127.1, 61.0 (CH_2), 14.3 (CH_3); *m/e* (EI) 298 (M^+), 253 (100), 225, 152.

4,4′-Difluorobiphenyl:[51] mp = 88−90 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.5 (dd, $J = 8.8$, 5.2 Hz, 4H), 7.1 (t(dd), $J = 8.8$, 8.8 Hz, 4H); *m/e* (CI NH_3) 190 (M^+), 171, 152.

4,4′-Dimethylbiphenyl:[56] mp = 119 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.48 (d, $J = 8$ Hz, 4H), 7.23 (d, $J = 8$ Hz, 4H), 2.38 (s, 6H); *m/e* (EI) 182 (M^+), 167 (100), 152.

2,2′-Dimethylbiphenyl:[57] ^1H NMR (250 MHz, $CDCl_3$) δ 7.19−7.10 (m, 6H), 7.02 (dd, $J = 6$, 1.5 Hz, 2H), 1.97 (s, 6H); *m/e* (EI) 182 (M^+), 167 (100), 152, 76.

4,4′-Di-*tert*-butylbiphenyl:[51] mp = 128−129 °C; ^1H NMR ($CDCl_3$) δ 7.5 (d, $J = 8.6$ Hz, 4H), 7.44 (d, $J = 8.6$ Hz, 4H), 1.36 (s, 18H).

2,2′-Dimethyl-1,1′-binaphthyl:[5b] ^1H NMR (200 MHz $CDCl_3$) δ 7.89 (d, $J = 8$ Hz, 2H), 7.87 (d, $J = 8$ Hz, 2H), 7.50 (d, $J = 8$ Hz, 2H), 7.39 (dd, $J = 7$, 1.2 Hz, 2H), 7.19 (dd, $J = 7$, 1.2 Hz, 2H), 7.04 (d, $J = 8$ Hz, 2H), 2.02 (s, 6H); *m/e* (EI) 282 (100, M^+), 267, 252, 126.

2-(Diphenylphosphinyl)naphthalene:[58] mp = 184−185 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 8.30 (d, $J_{PH} = 14$ Hz, 1H), 7.88 (d, $J = 8.5$ Hz, 2H), 7.72−7.68 (m, 4H), 7.65−7.44 (m, 10H); ^{31}P NMR ($CDCl_3$) δ 29.19; *m/e* (CI, NH_3) 329 (M + 1).

3-(Diphenylphosphinyl)-1-methoxybenzene: ^1H NMR (250 MHz, $CDCl_3$) δ 7.67−7.56 (m, 4H), 7.48−7.35 (m, 6H), 7.29 (td, $J = 7.8$ Hz, $J_{PH} = 4$ Hz, 1 H), 7.22 (broad d, $J_{PH} = 14.5$ Hz, 1 H), 7.07 (dd, $J_{PH} = 11$ Hz, 7.5 Hz, 1 H), 7.00 (dd, $J = 7.5$ Hz, $J_{PH} = 2.7$ Hz, 1 H), 3.72 (s, 3H); ^{31}P NMR ($CDCl_3$) δ 29.37; *m/e* (CI, NH_3) 309 (M + 1).

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(51) The spectra were compared to those of a commercial sample.

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