Quantitative Evaluation of the Factors Contributing to the "Copper Effect" in the Stille Reaction

Arturo L. Casado and Pablo Espinet*

*Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid,
E-47005 Valladolid, Spain*

The relative importance of the factors contributing to the accelerating effect of CuI on [PdL$_4$]-catalyzed couplings of R^{1}I and R^{2}SnBu$_3$ (*copper effect*) has been quantitatively evaluated in THF for R^1 = 3,5-C$_6$Cl$_2$F$_3$; R^2 = vinyl, C$_6$H$_4$-4-OMe; L = AsPh$_3$, PPh$_3$, using spectroscopic and kinetic methods. The ^{19}F NMR kinetic data show that the rate enhancement produced by addition of CuI is strongly related with the "autoretardation" effect intrinsic to [PdL$_4$] catalysts and is almost independent of the organotin reagent (vinyl, aryl). The "autoretardation" is due to the release of 2 equiv of L during the oxidation of [PdL$_4$] to yield *trans*-[PdR^{1}IL$_2$], which is the species undergoing transmetalation. CuI does not promote the dissociation of L from *trans*-[PdR^{1}L$_2$], but it captures part of the free neutral ligand L and therefore mitigates the autoretardation produced by the presence of free L on the rate-determining associative transmetalation. In the conditions studied (Pd:Cu = 1:2; T = 322.6 K; THF as solvent), for L = AsPh$_3$ the CuI added captures about 25% of the free AsPh$_3$ and the copper effect compensates only ca. 1% of the autoretardation, whereas for L = PPh$_3$ the CuI captures about 99% of the free PPh$_3$ and the compensation is about 30%. This remarkable variation is caused by the combined effect of two independent factors: (i) The catalyst [Pd(PPh$_3$)$_4$] is more autoretarded than [Pd(AsPh$_3$)$_4$]; and (ii) CuI is a more effective scavenger for PPh$_3$ than for AsPh$_3$.

Introduction

The Stille reaction (Pd-catalyzed coupling between organotins and organic electrophiles)[1] is complex and can follow different pathways depending on a number of factors such as the kind of electrophile, the solvent, the ancillary ligand, and the addition or not of LiCl. We have recently contributed to a better understanding of these factors, providing the frame of a dual mechanism shown in Scheme 1.[2−4]

The previous mechanistic conception implied predissociation of L and rate-limiting transmetalation on *trans*-[PdR^{1}XL] or *trans*-[PdR^{1}XL(solvent)] (X = halide).[5] Three important novelties in the modern conception are as follows: (i) The transmetalation is not always the rate-determining step (rds). (ii) The transmetalation is an associative ligand substitution on intermediates *trans*-[PdR^{1}YL$_2$] involving a pentacoordinate transition state **TS(A)** or **TS(B)**, and this has stereochemical consequences on the kind of Pd isomer produced after the transmetalation. (iii) For transmetalations of chiral α-carbons the outcome of the reaction can be retention (upper cycle) or inversion (lower cycle) of configuration, a kind of dual result reported in the literature,[6,7] difficult to accommodate in the old dissociative model.
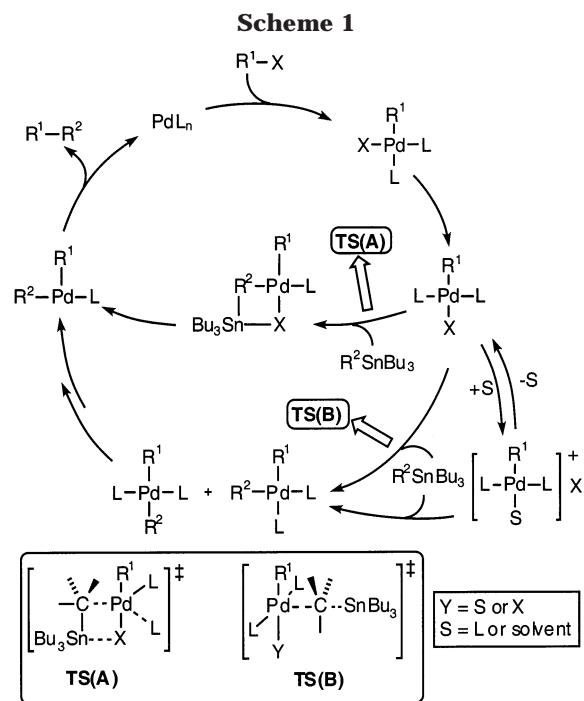
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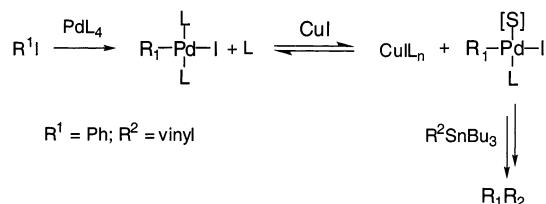
Scheme 1

According to our previous results, the rds in the conditions we are concerned with in this article (Y = I, solvent = THF) is the transmetalation, while the oxidative addition is fast. The reaction follows the upper

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Scheme 2

Scheme 3

$R^1 = Ph; R^2 = vinyl$
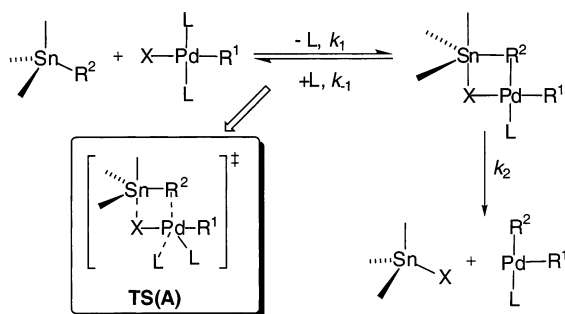
cycle via a cyclic transition state **TS(A)**. The transmetalation produces an R^2-for-L substitution, releasing 1 mol of the leaving ligand L and leading to a *cis*-PdR^{1}R^2 arrangement in the product. Since the reaction rate is determined by the transmetalation step (Scheme 2), it shows an inverse dependence on [L] (eq 1), which can mislead one to the conclusion of a transmetalation involving a dissociative preequilibrium, as discussed elsewhere.[8]

$$r_{obs} = k_{obs}[R^2SnBu_3] = \frac{k_1 k_2 [PdR^1IL_2]}{k_{-1}[L] + k_2}[R^2SnBu_3] \quad (1)$$

A remarkable phenomenon in Stille couplings is the effect of the addition of CuI or other Cu(I) salts, which are known to accelerate with variable success the couplings catalyzed by [PdL$_4$].[5,7,9–16] This so-called "copper effect" has been studied before by the groups of Farina and Liebeskind.[17] Within the frame of the predissociation mechanism for the transmetalation, accepted at that moment, they concluded that the role of CuI in front of "strong" ligands such as PPh$_3$ is to scavenge free ligand. The latter is detrimental for the transmetalation because it inhibits dissociation (Scheme 3). It was also suggested that for "soft" ligands (such as AsPh$_3$) ligand dissociation from Pd(II) is not a problem,
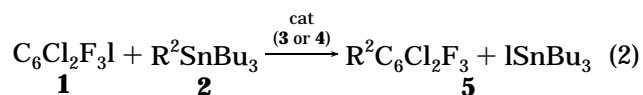
and this is why addition of CuI produces minimal rate accelerations.

The modern associative scheme can accommodate this explanation easily by changing the concept "L predissociation" for "L associative substitution" on a square planar Pd(II), since the associative transmetalation is equally retarded by free ligand. A conceptual difference is that scavenging free ligand in the dissociative scheme implies increasing the concentration of species supposed to undergo transmetalation ([PdR^{1}IL(S)]), whereas in the associative mechanism it does not imply change in concentration of the species actually undergoing transmetalation (*trans*-[PdR^{1}IL$_2$]).[8] In the associative scheme the two obvious factors contributing to the different behavior of PPh$_3$ and AsPh$_3$ are the different values of k_1 and k_{-1} in eq 1 for the two ligands and also the different affinity of Cu(I) for them. We thought it should be interesting to try to quantify the effect and do it separately for the two factors, taking advantage of our experience in the use of stable palladium fluoroaryl derivatives for kinetic studies and the facility of observation associated with ^{19}F NMR spectroscopy. The results are presented here.

The reader should be aware that the effect studied in this paper is not the only possible role of copper salts. In their initial study Farina and Liebeskind already proposed that in very polar solvents a Sn/Cu transmetalation was taking place (i.e., organocopper species were participating in the reaction), a proposal recently developped into an effective coupling system for sterically congested substrates.[16] In fact copper-mediated cross-coupling of organostannanes with organic electrophiles in mild conditions (usually in polar solvents) is now a useful synthetic method.[18–23]

Results and Discussion

Catalytic Activity of *trans*-[Pd(C$_6$Cl$_2$F$_3$)IL$_2$] (L = PPh$_3$, AsPh$_3$) without CuI. It has been established before that the transmetalation step is rate determining for the catalytic coupling of aryl or vinyl stannanes and aryl iodide in THF.[2,5,9] The coupling of C$_6$Cl$_2$F$_3$I (**1**) with R^{2}SnBu$_3$ (R^2 = vinyl, **2a**; 4-anisyl, **2b**) catalyzed by [Pd(PPh$_3$)$_4$] does not occur at a detectable rate: Although the initial oxidative addition gives [Pd(C$_6$Cl$_2$F$_3$)I(PPh$_3$)$_2$] + 2 PPh$_3$, the subsequent transmetalation step does not proceed in the presence of such excess of free PPh$_3$. Thus, to compare the ligand influence on the kinetic behavior of PPh$_3$- and AsPh$_3$-based catalysts, we have studied the coupling catalyzed by *trans*-[Pd(C$_6$Cl$_2$F$_3$)I(PPh$_3$)$_2$] (**3**) in THF in the presence of various smaller proportions of added PPh$_3$. The reactions were clean, and no byproducts were observed. The products C$_6$Cl$_2$F$_3$–R^2 (R^2 = vinyl, **5a**; 4-anisyl, **5b**) were formed in up to 95% yield (eq 2). The decay of [**1**] (monitored by ^{19}F NMR) followed first-order kinetics.

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$$C_6Cl_2F_3I + R^2SnBu_3 \xrightarrow[\text{(3 or 4)}]{\text{cat}} R^2C_6Cl_2F_3 + ISnBu_3 \quad (2)$$
$$\textbf{1} \qquad\quad \textbf{2} \qquad\qquad\qquad \textbf{5}$$

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Table 1. First-Order Rate Constants, k_{obs}, for the Coupling of $C_6Cl_2F_3I$ (1) and $Sn(vinyl)Bu_3$ (2a) Catalyzed by *trans*-[Pd($C_6Cl_2F_3$)I(PPh$_3$)$_2$] (3) in THF[a]

T/K	$[PPh_3]_{added}/10^{-3}$ mol L^{-1}	$k_{obs}/10^{-5}$ s^{-1}
328.5 ± 0.2	0	1.44 ± 0.04
322.6	0.273 ± 0.009	0.233 ± 0.009
322.6	0.164 ± 0.005	0.42 ± 0.02
322.6	0.065 ± 0.002	0.92 ± 0.03
322.6	0	0.99 ± 0.04
317.1	0	0.685 ± 0.010
311.3	0	0.386 ± 0.018
305.9	0	0.247 ± 0.008
299.9	0	0.139 ± 0.006
295.8	0	0.099 ± 0.006

[a] $[1]_0 = [2a]_0 = (2.000 \pm 0.017) \times 10^{-1}$ mol L^{-1}, $[3] = (1.00 \pm 0.03) \times 10^{-2}$ mol L^{-1}. Data for the reaction catalyzed by *trans*-[Pd($C_6Cl_2F_3$)I(AsPh$_3$)$_2$] (**4**) are reported in ref 2.

The k_{obs} values found for the different concentrations of added PPh$_3$ are given in Table 1. The results are compared with those obtained previously using *trans*-[Pd($C_6Cl_2F_3$)I(AsPh$_3$)$_2$] (**4**).[2] An analysis of the data reveals two major kinetic differences between the two catalysts:

(i) The reaction catalyzed by complex **4** is about 40 times faster than using **3**. Since the entropic and steric factors should be very similar,[24] the variation in rates must be mainly due to differences in activation enthalpy. In effect, an Eyring treatment of k_{obs} in the range 295−330 K yields $\Delta H^\ddagger = 65.1 \pm 1.4$ kJ mol^{-1} and $\Delta S^\ddagger = -139 \pm 5$ J K^{-1} mol^{-1} for the reaction catalyzed by **3**, compared to $\Delta H^\ddagger = 50 \pm 2$ kJ mol^{-1} and $\Delta S^\ddagger = -155 \pm 7$ J K^{-1} mol^{-1} for the reaction catalyzed by **4**.[2] Both activation entropy values are in the range of those found for other associative ligand substitutions in Pd(II) complexes.[25] This supports an associative transmetalation mechanism involving a pentacoordinated palladium(II) transition state, as proposed in Scheme 1 (upper cycle). The difference in activation enthalpy for **3** and **4** reflects two main contributions: (a) Complex *trans*-[PdR^{1}I(AsPh$_3$)$_2$] is more electrophilic than *trans*-[PdR^{1}I(PPh$_3$)$_2$] (because PPh$_3$ is a stronger donor); and (b) the elongation (and the eventual scission) of the bond to the leaving ligand, Pd−L, is easier for L = AsPh$_3$, because the Pd−P bond is stronger than Pd−As. We have not found data for these bond energies in the literature, but the expected effect is that if Pd−PPh$_3$ is the stronger bond, it should be preferred to Pd−AsPh$_3$. This is a well-documented fact: [PdR$_2$(AsPh$_3$)$_2$] and [PdRX(AsPh$_3$)$_2$] complexes are general precursors for complexes with many other L ligands (including L = PPh$_3$) by associative ligand substitution reactions,[26] whereas PPh$_3$ is hardly displaced by other ligands from similar PPh$_3$ complexes.

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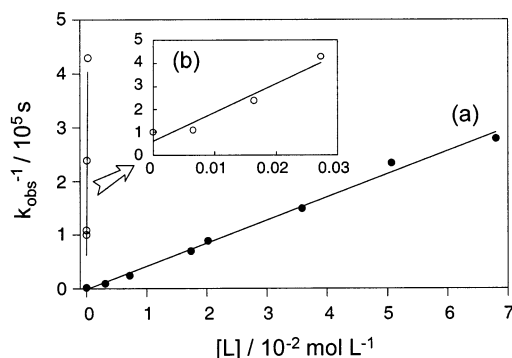
Figure 1. k_{obs}^{-1} vs $[L]_{added}$ plots for the couplings of $C_6Cl_2F_3I$ (**1**, 0.2 mol L^{-1}) and $Sn(vinyl)Bu_3$ (**2a**, 0.2 mol L^{-1}) catalyzed by *trans*-[Pd($C_6Cl_2F_3$)IL$_2$] (0.01 mol L^{-1}) in THF at 322.6 K: (a) L = AsPh$_3$; (b) L = PPh$_3$. Values for L = AsPh$_3$ have been taken from ref 2.

(ii) The coupling retardation by addition of L is very swift for **3** and temperate for **4**. In both cases, the reaction is minus first-order in the concentration of added L. The linear plots k_{obs}^{-1} vs $[L]_{added}$ are shown in Figure 1. The slopes are $(1.54 \pm 0.13) \times 10^9$ L s mol^{-1} for **3** and $(4.31 \pm 0.17) \times 10^6$ L s mol^{-1} for **4**. That is, the coupling catalyzed by **3** is retarded by L over 2 orders of magnitude more quickly than that catalyzed by **4**.

Catalytic Activity of *trans*-[Pd($C_6Cl_2F_3$)IL$_2$] (L = PPh$_3$, AsPh$_3$) with 2 CuI + 2 L. The kinetic effect of CuI in these systems was estimated from the measurements described now. First, we determined the observed rate constant K'_{obs} for eq 2 using as catalyst a mixture of the Pd complex (**3** or **4**) and 2 equiv of L per Pd (a mixture complex:L = 1:2 should be catalytically equivalent to the system produced once the oxidative addition has taken place in a catalysis with [PdL$_4$]).[27] On the other hand, we measured the rate constant k''_{obs} for eq 2 using as catalyst a mixture (**3** or **4**):L:CuI = 1:2:2 (this catalytic mixture is equivalent to a mixture of [PdL$_4$] and 2 equiv of CuI). These observed rate constants are compared with the observed rate constants measured in the absence of added L or CuI (k^0_{obs}, taken from Table 1 and from ref 2). The results are shown in Table 2. In the last column of Table 2 we collect the value of the quotient $(K''_{obs} - K'_{obs})/(k^0_{obs} - K'_{obs})$. Since the autoretardation is a consequence of the release of 2 equiv of L when [PdL$_4$] enters the catalytic cycle and is transformed into *trans*-[PdR^{1}IL$_2$], $(k''_{obs} - K'_{obs})/(k^0_{obs} - K'_{obs})$ is an estimation of the ratio between the rate enhancement achieved by addition of CuI to couplings catalyzed by [PdL$_4$] ($k'_{obs} - K'_{obs}$) and the autoretardation effect in these catalyses ($k^0_{obs} - K'_{obs}$). In other words the quotient estimates the fraction of autoretardation compensated by CuI. For L = PPh$_3$ the addition of CuI compensates about 30% of the autoretardation, whereas for L = AsPh$_3$, the compensation is only about 1%. For L = PPh$_3$ the effect is almost independent of the organotin reagent, suggesting that the involvement of organocopper species in the rate enhancement is insignificant, as expected in low polar solvents and with strong ligands from the study by Farina and Liebes-

(27) This procedure facilitates the kinetic study because it obviates the induction period for catalysts activation.

**Table 2. Determination of the Copper Effect in Couplings of $C_6Cl_2F_3I$ (1) with R^2SnBu_3 (2a,b) Catalyzed by
trans-[Pd($C_6Cl_2F_3$)IL₂] (3, 4)[a]**

R^2	L	$k^0_{obs}/10^{-5}$ s^{-1}	$K_{obs}/10^{-5}$ s^{-1}	$K'_{obs}/10^{-5}$ s^{-1}	$(K'_{obs} - K_{obs})/(k^0_{obs} - K_{obs})$
vinyl	AsPh₃	33.7 ± 0.4	1.12 ± 0.03	1.60 ± 0.03	0.015 ± 0.001
vinyl	PPh₃	0.99 ± 0.04	≈0	0.311 ± 0.005	0.314 ± 0.014
aryl	AsPh₃	1.94 ± 0.02	0.118 ± 0.02	0.122 ± 0.02	0.002 ± 0.016
aryl	PPh₃	0.054 ± 0.002	≈0	0.016 ± 0.002	0.30 ± 0.04

[a] $[1]_0 = [2]_0 = (2.000 ± 0.017) \times 10^{-1}$ mol L^{-1}, [3] or [4] = $(1.00 ± 0.03) \times 10^{-2}$ mol L^{-1}, THF, 322.6 K. See definition of k^0_{obs}, K_{obs}, and K'_{obs} in the text.

kind.[17,28] For L = AsPh₃ the values measured are small and the error is significant, precluding to be conclusive in this respect.

In separate experiments, complexes **3** and **4** did not react noticeably with CuI under the experimental conditions used in the catalytic couplings (1×10^{-2} mol L^{-1}, THF, 322 K). No new Pd species were observed by ^{19}F or ^{31}P NMR. Therefore, CuI is not able to extract L from *trans*-[PdR^{1}IL₂] (L = PPh₃, AsPh₃) to a perceptible extent.[29] However, it captures efficiently free neutral ligand L and mitigates the intrinsic autoretardation of this catalytic system (eq 3).

$$trans\text{-}[Pd(C_6Cl_2F_3)IL_2] + 2\ L + 2\ CuI \rightleftharpoons$$
$$trans\text{-}[Pd(C_6Cl_2F_3)IL_2] + 2\ [CuIL]\quad (3)$$
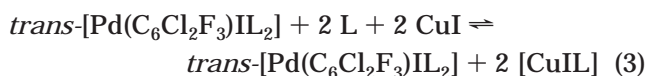
Based on this model, an estimation of the concentration of free ligand L in a catalytic mixture containing (**3** or **4**):L:CuI = 1:2:2 can be made from the kinetic data entering the value of K'_{obs} from Table 2 into the kinetic plot in Figure 1. For **4**, the concentration of free AsPh₃ is 1.5×10^{-2} mol L^{-1}. This means that CuI captures ca. 25% of the AsPh₃ released after the oxidative addition on [Pd(AsPh₃)₄]. In the case of **3**, the concentration of free PPh₃ is 2.1×10^{-4} mol L^{-1}; that is, CuI captures ca. 99% of the PPh₃ released from [Pd(PPh₃)₄] by oxidative addition of IR.[1]

^{31}P NMR Experiments on CuI/L Systems. The question arises whether the capture of L by CuI is fast enough compared to the transmetalation. The dynamics of [CuIL]/CuI/L systems was studied independently by ^{31}P NMR under conditions similar to those used in catalytic couplings. The spectrum of a 0.02 mol L^{-1} solution of PPh₃ (THF, 322 K) showed a sharp singlet at −0.30 ppm. This peak disappeared immediately upon addition of 1 equiv of CuI (the ^{31}P NMR spectrum of an original sample of [CuI(PPh₃)] (**5**) is also flat). This experiment indicates that the reaction between PPh₃

and CuI, to yield [CuI(PPh₃)],[30] is fast compared to the transmetalation in the Stille cycle. A second spectrum recorded after addition of an additional 1 equiv of PPh₃ (CuI:PPh₃ = 1:2) showed only one broad signal at −3.17 ppm. This signal became sharper and shifted toward the position of free PPh₃ upon successive additions of PPh₃ to the mixture ($\delta = -1.00$ ppm for Cu:PPh₃ = 1:4; $\delta = -0.38$ ppm for Cu:PPh₃ = 1:7). From these results, it seems that CuI in THF can take more than one PPh₃ and form adducts [CuI(PPh₃)$_n$] or [CuI(PPh₃)$_n$(THF)$_m$].[31,32] Moreover, the observation of only one broad signal suggests a fast exchange between free and coordinated PPh₃ (eq 4).[33]

$$[CuI(PPh_3)_{n-1}(THT)_m] + PPh_3 \rightleftharpoons$$
$$[CuI(PPh_3)_n(THT)_{m-1}] + THT\quad (4)$$
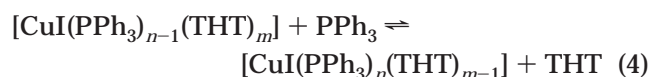
Competition experiments were carried out to further compare the affinity of CuI for PPh₃ versus AsPh₃. Treating a 0.02 mol L^{-1} sample of PPh₃ with 1 equiv of [CuI(AsPh₃)] (**6**) (THF, 322 K), the ^{31}P NMR signal for free PPh₃ quickly vanished, suggesting that all the PPh₃ was trapped by CuI (eq 5). The peak for free PPh₃ was not recovered after addition of 50 equiv of AsPh₃, revealing that the coordinated PPh₃ was not substituted significantly in the presence of that huge excess of arsine and suggesting that the affinity of CuI is more than 50-fold higher for PPh₃ than for AsPh₃. This behavior is consistent with the estimations drawn from the kinetic data discussed before.

$$[CuI(AsPh_3)] + PPh_3 \rightarrow [CuI(PPh_3)_n(AsPh_3)_m]\quad (5)$$

Conclusion

CuI does not promote the dissociation of L from *trans*-[PdR^{1}IL₂], but it captures part of the free neutral ligand L released during the oxidation of [PdL₄] that yields the species actually undergoing transmetalation, *trans*-[PdR^{1}IL₂], plus 2 L. Therefore CuI mitigates the "autoretardation" produced by the presence of free L on the rate-determining associative transmetalation. In the conditions studied (Pd:Cu = 1:2; THT as solvent), for L

(28) This is also supported by the fact that the Stille couplings in Table 2, carried out with Cu(I) species, were very clean and no byproducts were detected. As an exception, ca. 5% mol of (C₆Cl₂F₃)-SnBu₃ (**2c**) was formed when the coupling between **1** with **2a** (R² = vinyl) was catalyzed by *trans*-[Pd(C₆Cl₂F₃)I(PPh₃)₂] (**3**), CuI, and PPh₃. This reaction is very slow (25 h at 322 K in THF, and we have observed sometimes the formation of this byproduct in other slow reactions in the absence of CuI (P. Espinet and Ana Gallego, unpublished results. See also ref 3). Due to this observation, the participation of organo-copper derivatives to a small extent cannot be fully excluded in this reaction.

(29) No new product was observed by ^{19}F and ^{31}P{^{1}H} NMR after mixing *trans*-[Pd(C₆Cl₂F₃)IL₂] (L = PPh₃, AsPh₃) and CuI at 50 °C in THF. In the case of L extraction by CuI or in the case of spontaneous predissociation (see ref 8), the known dimer [Pd₂(C₆Cl₂F₃)₂(μ-I)₂L₂] should be formed. For L = PPh₃, traces of the dimer, along with OPPh₃, were detected due to oxidation by air, but these were formed in similar amounts in a control experiment in the absence of CuI.

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(32) Tetracoordinated Cu(I) complexes are common. See: Hattaway, B. J. Copper, section 53.3. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 5.

(33) The ^{63}Cu quadrupolar relaxation mechanism may also contribute to the fast relaxation of phosphorus nuclei, giving broad signals: Pregosin, P. S., Ed. *Transition Metal Nuclear Magnetic Resonance*; Elsevier: Amsterdam, 1991.

= AsPh$_3$ the CuI added captures about 25% of the free AsPh$_3$ and the copper effect compensates only ca. 1% of the autoretardation. For L = PPh$_3$ the CuI captures about 99% of the free PPh$_3$ and the compensation is about 30%. This variation is caused by the combined effect of two independent factors: (i) The catalyst [Pd-(PPh$_3$)$_4$] is more autoretarded than [Pd(AsPh$_3$)$_4$]; and (ii) CuI is a more effective scavenger for released PPh$_3$ than for released AsPh$_3$. It is of little use to add CuI when L = AsPh$_3$, at least for the purpose of rate acceleration. The coupling of aryl iodides and stannanes catalyzed by [PdL$_4$] is faster for L = AsPh$_3$, even in the absence of CuI, than for L = PPh$_3$ with CuI added.

Experimental Section

The preparation of C$_6$Cl$_2$F$_3$I (**1**), R^{2}SnBu$_3$ (R^2 = vinyl, **2a**; 4-anisyl, **2b**), *trans*-[Pd(C$_6$Cl$_2$F$_3$)I(AsPh$_3$)$_2$] (**4**), and C$_6$Cl$_2$F$_3$–R^2 (R^2 = vinyl, **5a**; 4-anisyl, **5b**) is reported in ref 2.

CuIL (L = PPh$_3$, 5; AsPh$_3$, 6). A solution of AsPh$_3$ (161 mg, 0.526 mmol) in MeCN (2 mL) was added to a solution of CuI (100 mg, 0.525 mmol) in the same solvent (10 mL) under N$_2$. After a few seconds complex **6** started to precipitate. The mixture was stirred for 1 h, and the solid was filtered, washed with MeCN, and vacuum-dried (yield 225 mg, 87%): IR (KBr) 1482 (s), 1434 (vs), 1079 (s), 741 (vs), 694 (vs), 470 (s). Anal. Calcd for C$_{18}$H$_{15}$AsCuI: C, 43.53; H, 3.04. Found: C, 43.35; H, 2.97. Compound **5** was similarly prepared from PPh$_3$ (yield 97%): IR (KBr) 1479 (s), 1434 (vs), 1097 (vs), 748 (vs), 695 (vs), 521 (vs), 503 (s). Anal. Calcd for C$_{18}$H$_{15}$CuIP: C, 47.75; H, 3.34. Found: C, 47.48; H, 3.23.

Kinetic Experiments on Pd-Catalyzed Couplings of C$_6$Cl$_2$F$_3$I with Organotributyltins; Reactions of Organopalladium(II), Organotributyltins, and [CuIL] Complexes. These NMR experiments were carried out as described previously for similar cases.[2]

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