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Stille Coupling of Alkynyl Stannane and Aryl Iodide, a Many-Pathways Reaction: The Importance of Isomerization

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The kinetics of the Stille reaction between $C_6Cl_2F_3I$ and $PhCCSnBu_3$ have been studied for the whole catalytic system and for transmetalations as separate steps. The use of (trifluorodichlorophenyl)-palladium derivatives slows down the reactions and allows for the observation of the intermediates *cis*- and *trans*-$[Pd(C_6Cl_2F_3)I(PPh_3)_2]$. The first is formed in the oxidative addition step and isomerizes to the second. Both were studied as catalysts for the whole cycle. The kinetic study compares the relevance of the transmetalation step on each isomer. The competing transmetalations produce both *cis*- and *trans*-$[Pd(C_6Cl_2F_3)(PhCC)(PPh_3)_2]$. The former undergoes very fast C−C coupling, while the second accumulates in solution due to extremely slow isomerization. Thus, the system is a case study of the effect of competing pathways in the Stille reaction and its consequences on the performance of the catalytic process.

Introduction

Among the mechanisms of palladium-catalyzed cross-coupling processes, that of the Stille reaction is perhaps the most studied experimentally.[1,2] A comprehensive account of mechanistic studies was published in 2004.[3] The possible general pathways for the process are summarized in Scheme 1. The steps preceding the transmetalation have been experimentally confirmed by observation or unambiguous kinetic deduction of intermediates.[4−6] Further studies,[7−9] including detailed theoretical (DFT) calculations[10−12] and the observation of a post-transmetalation intermediate, $[PdR^1R^2(AsPh_3)(ISnBu_3)]$,[10] identified during the study of the retro-transmetalation reaction on *cis*-$[PdRf_2(AsPh_3)_2]$ ($R^1 = R^2 = Rf = 3,5\text{-}C_6Cl_2F_3$),[13,14] have been published more recently.

Obviously, the basic Scheme 1 needs to be adjusted to include particular cases. For instance, coordinating solvents can partially replace ligands in some reaction intermediates.[5,15] If a chelating ligand is used, the thermodynamic products of the oxidative addition and therefrom should be cis, rather than the trans structures depicted in Scheme 1. Observation of these chelated intermediates has been reported,[4] and in one case the process has been mechanistically studied using NMR and UV/vis techniques.[16,17] With bulky ligands most intermediates will be tricoordinated instead of tetracoordinated, as proposed recently by calculation and by some experiments.[18]

Further variations to be considered, in the case of monodentate ligands, are the stereochemistry of the initial oxidative addition product and the cis to trans isomerization rate, as compared to that of transmetalation (both rates will depend on each particular case). The oxidative addition has been thoroughly studied both theoretically and experimentally, and two possible pathways are accepted: the three-center mechanism that leads to *cis*-$[PdRXL_2]$[19] and an ionic mechanism that leads to *trans*-$[PdRXL_2]$.[19a,b,20] When the cis to trans isomerization reaction is comparatively fast, the fugacious existence of the isomer *cis*-$[PdRXL_2]$ is irrelevant. When this is not the case and *cis*-$[PdRXL_2]$ is produced

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(14) For "retrotransmetalation" we mean the exchange of an R on Pd for an X on Sn, the reverse of what happens in the so-called transmetalation.
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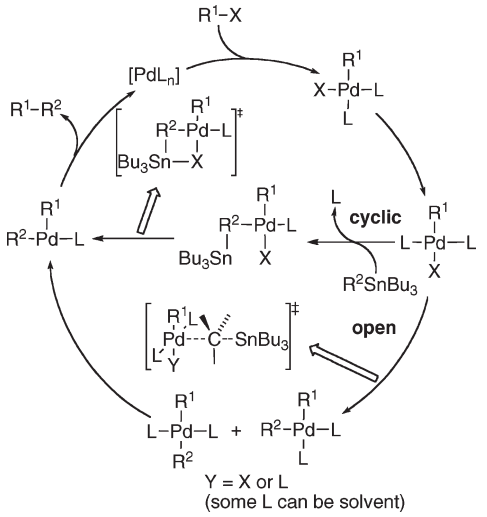
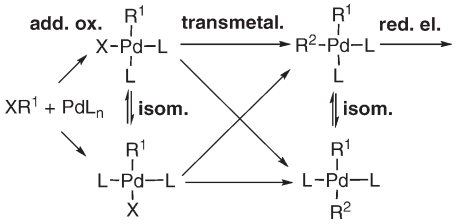
Scheme 1



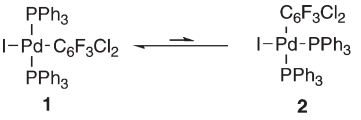
Scheme 2



upon oxidative addition, the transmetalation on *cis*- and *trans*-[PdRXL$_2$] intermediates needs to be considered. Then, the transformations depicted in Scheme 2 have to be taken into account. In this paper we study a case where this competition of transmetalations on *cis*- and *trans*-[PdRXL$_2$] complexes is actually observed.

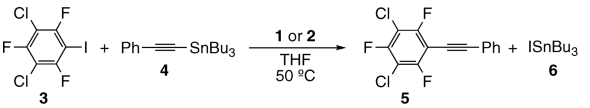
Results and Discussion

During preliminary experiments of a kinetic study, using *trans*-[PdRfI(PPh$_3$)$_2$] (**1**) as catalyst, of the C−C coupling of RfI (Rf = $C_6Cl_2F_3$) (**3**) and PhC≡CSnBu$_3$ (**4**) we detected, at variance with other studies on related systems, the presence of *cis*-[PdRfI(PPh$_3$)$_2$] (**2**). This complex is an oxidative addition intermediate, assumed to occur but not detected in catalytic conditions in our previous studies. Thermodynamically, *cis*-[PdRfI(PPh$_3$)$_2$] is unstable and isomerizes completely to the trans isomer (eq 1),[21] but its detection under catalytic conditions makes it kinetically and mechanistically significant for the reaction. Since the complexes *cis*- and *trans*-[PdRfI(PPh$_3$)$_2$] can both be isolated,[21] this system offers a rare chance to study the transmetalation and the catalytic cycle starting on each isomer **1** or **2**. Additionally, the use of PhC≡CSnBu$_3$ provides a higher stability of the resulting alkynylpalladium intermediates compared to their vinyl or aryl analogues[22] and facilitates its observation.



(1)

The Pd-catalyzed reaction of RfI with (phenylethynyl)-tributyltin in THF at 50 °C proceeds as expected for a Stille process, affording the coupling product PhC≡CRf (**5**) and ISnBu$_3$ (**6**) (eq 2). The reaction is very slow at this temperature and can be followed in the course of the first few hours by NMR techniques, allowing for the observation of mechanistically informative intermediates, as well as some byproducts that are also analyzed below.



(2)

Monitoring the Catalytic Reactions. As most of the compounds involved in the catalysis studied contain $C_6F_3Cl_2$, ^{19}F NMR monitoring affords interesting information. The reaction using *trans*-[PdRfI(PPh$_3$)$_2$] (**1**) as the initial catalyst, in THF at 50 °C, showed that during the reaction compound **1** was partially replaced by two other palladium complexes (Figure 1). One of them, *cis*-[PdRfI(PPh$_3$)$_2$] (**2**), is the kinetic oxidative addition product of **3** to Pd(PPh$_3$)$_n$ intermediates. The other was identified as *trans*-[PdRf(C≡CPh)(PPh$_3$)$_2$] (**7**), a transmetalation product. For its unambiguous identification, complex **7** was independently synthesized from PhC≡CSnBu$_3$ and *trans*-[PdRf(OTf)(PPh$_3$)$_2$][5] in THF at 0 °C, isolated, and fully characterized.

Throughout the catalysis depicted in Figure 1, the sum of concentrations of the Pd(II) complexes (**1** + **2** + **7**) remained constant,[23] as no metallic palladium was detected for the first hours of reaction, when there is still a large excess of the reagents. The formation of some small but steadily increasing SnRfBu$_3$ (**8**) side product was also detected during the reactions. This side product arises from undesired transmetalations.[24] It is worth noting that the amount of complex **7** continuously increased during the reaction, and the evolution of the concentrations of **1** and **2** came, after about 2 h, to a quasi-equilibrium, after which the ratio **1**:**2** remained almost constant,[25] while their total amount decreased steadily but slowly.

The observation of *cis*-[PdRfI(PPh$_3$)$_2$] (**2**) during the catalysis is remarkable and shows that, under the reaction

(19) For cases of oxidative addition to neutral Pd(0) complexes by a concerted mechanism see: (a) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434–442. (b) Bickelhaupt, F. M.; Ziegler, T.; Schleyer, P. v. R. *Organometallics* **1995**, *14*, 2288–2296. (c) Senn, H. M.; Ziegler, T. *Organometallics* **2004**, *23*, 2980–2988. (d) Ariafard, A.; Lin, Z. *Organometallics* **2006**, *25*, 4030–4033. (e) Lam, K. C.; Marder, T. B.; Lin, Z. *Organometallics* **2007**, *26*, 758–760. (f) Li, Z.; Fu, Y.; Guo, Q.-X.; Liu, L. *Organometallics* **2008**, *27*, 4043–4049. (g) Schoenebeck, F.; Houk, K. N. *J. Am. Chem. Soc.* **2010**, *132*, 2496–2497.

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(23) The metalated $C_6Cl_2F_3$ groups can be observed easily, as their ^{19}F chemical shifts are very different from those in organic molecules: Casares, J. A.; Espinet, P.; Martín-Alvarez, J. M.; Martínez-Ilarduya, J. M.; Salas, G. *Eur. J. Inorg. Chem.* **2005**, 3825–3831.

(24) Fuentes, B.; García-Melchor, M.; Lledós, A.; Maseras, F.; Casares, J. A.; Ujaque, G.; Espinet, P. *Chem. Eur. J.* **2010**, *16*, 8596–8599.

(25) Strictly it is not a true equilibrium because of the continuous and irreversible formation of complex **7**.

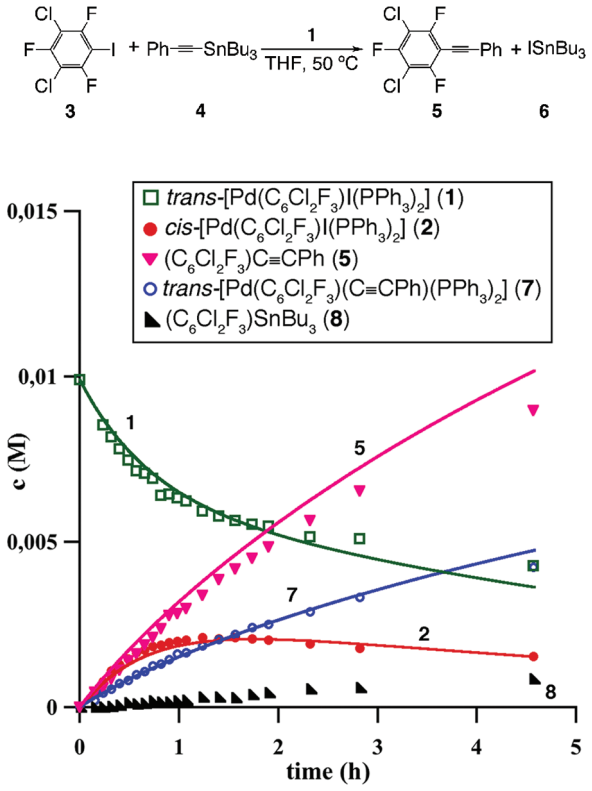


Figure 1. Concentration/time data for the reaction **3** + **4**, in THF at 323 K, using **1** as catalyst. Starting conditions; [**1**] = 0.01 M; [**3**] = [**4**] = 0.20 M. Note that the disappearance of **3** is not depicted and is far above the drawing limits. Solid lines represent the best nonlinear fitting.

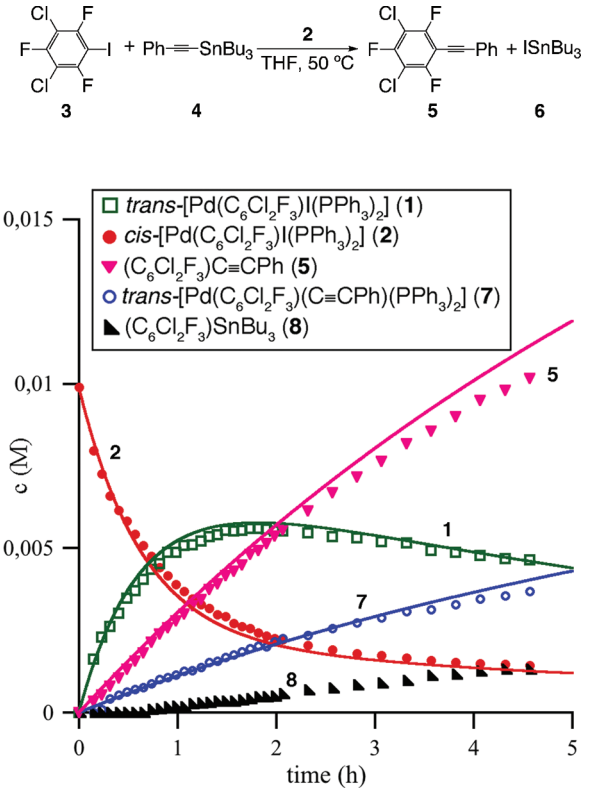


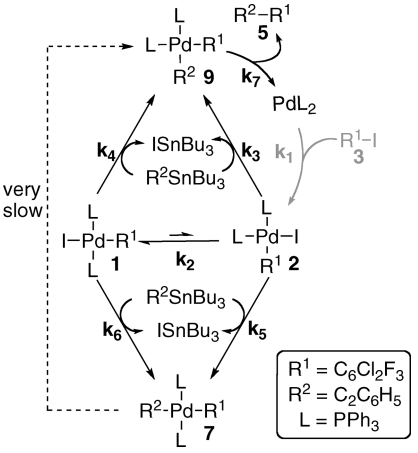
Figure 2. Concentration/time data for the reaction **3** + **4**, in THF at 323.2 K, using **2** as catalyst. Starting conditions: [**2**] = 0.01 M; [**3**] = [**4**] = 0.20 M. Note that the disappearance of **3** is not depicted and is out of the drawing limits. Solid lines represent the best nonlinear fitting.

conditions, it is formed by oxidative addition more rapidly than it disappears by isomerization to **1** (the trans complex is the thermodynamic product) or by transmetalation. Thus, in contrast with the reaction of **3** with Sn(vinyl)Bu_3, previously studied and reported,[6] where only **1** was observed during the catalysis, it is expected here that **2** might compete with **1** as catalyst (that is, as the compound undergoing transmetalation). Consequently, the coupling reaction was also studied and monitored using **2** as the initial catalyst (Figure 2). Again, as it happened starting from catalyst **1**, the system converged toward a quasi-equilibrium between complexes **1** and **2** while the concentration of **7** steadily increased.

The observations made so far show that the choice of initial catalyst **1** or **2** hardly affects the bulk result of the catalysis or the nature and relative amount of the palladium complexes observed, because a quasi-steady **1**:**2** ratio is reached soon in both cases. In other words, the overall catalyzed reaction will take place almost at the same rate and to the same extent, irrespective of the isomer **1** or **2** chosen as starting catalyst.

The expected products of direct transmetalation on **1** or **2** are *trans*-[PdRf(C≡CPh)$(PPh_3)_2$] (**7**) and *cis*-[PdRf(C≡CPh)-$(PPh_3)_2$] (**9**). The former is actually observed as a rather persistent product in solution; the second is not observed under the reaction conditions, suggesting that, when formed, it immediately undergoes C−C coupling to give **5**, as observed before for a similar system.[6] The synthesis of **9** was attempted by different methods, but **9** was never detected: even at low temperature (223 K) only the coupling product was observed, supporting the ephemeral nature of the putative intermediate **9**.

Scheme 3



The reductive elimination of **7** was monitored by ^{19}F NMR in separate experiments. It couples quickly in solution, when isolated, but the coupling is fairly efficiently quenched in the presence of PhC≡$CSnBu_3$ or PPh_3 in the reaction medium (as under catalytic conditions) and becomes very slow.[26]

(26) For the concentration used in catalysis, about 90% of the coupling product is formed in 3 h. The reaction has an induction time, which suggests that probably the reaction is initiated only after some phosphine oxidation favoring dissociation has occurred. This ligand dissociation can be compensated in the presence of other external coordinating species that exist under catalytic conditions (e.g., alkynyl in large excess). Thus, under the conditions of Figures 1 and 2 the coupling is less than 5% in 3 h.

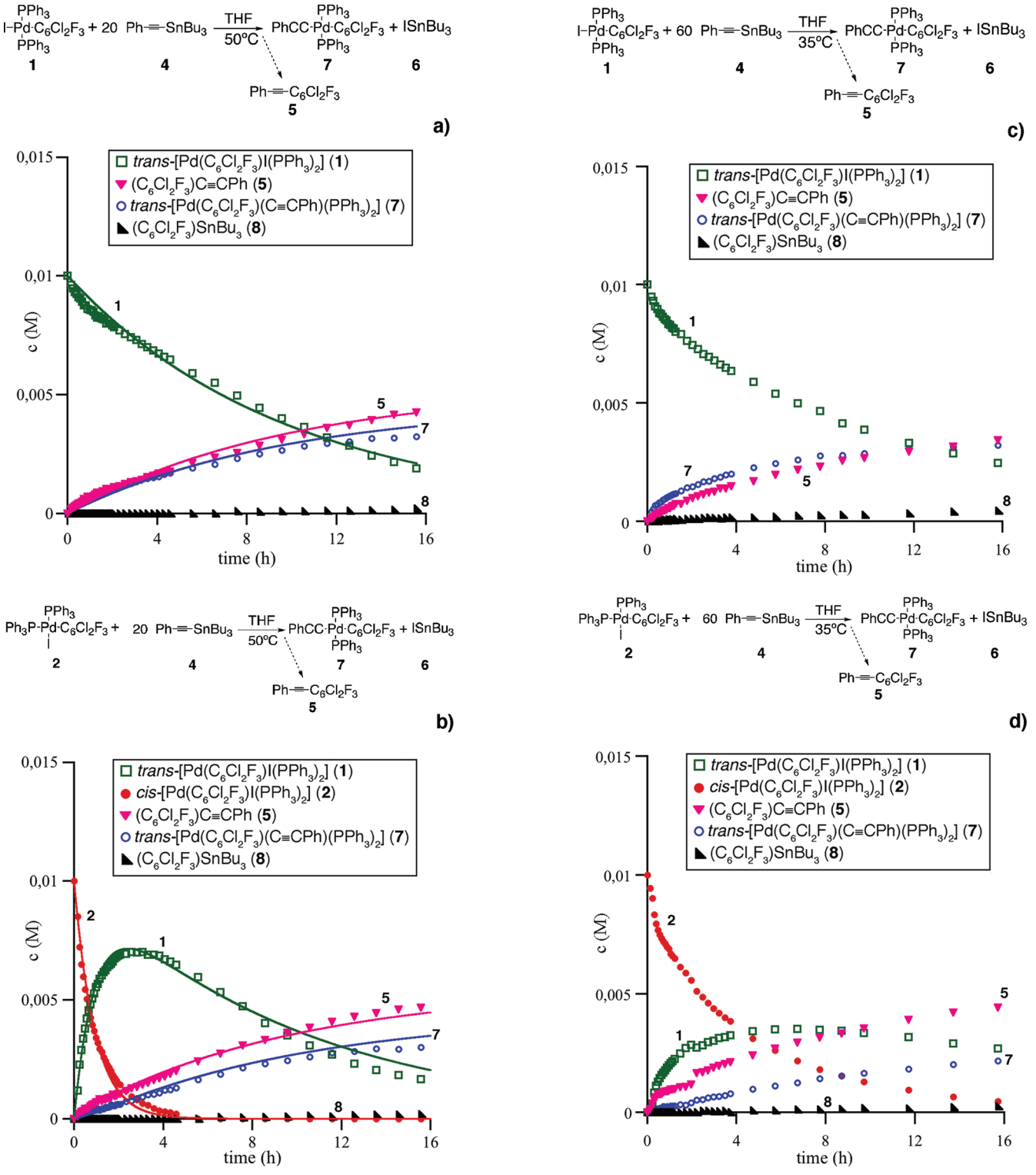
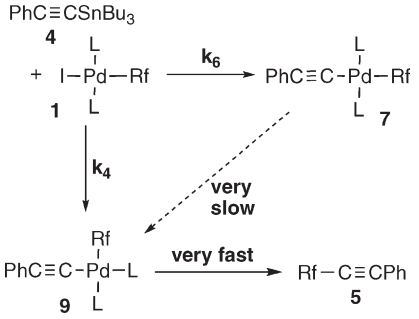


Figure 3. Concentration/time data for the transmetalation step obtained by ^{19}F NMR, in THF. Starting conditions: (a) $T = 323$ K, [**1**] = 0.01 M, [**4**] = 0.20 M; (b) $T = 323$ K, [**2**] = 0.01 M, [**4**] = 0.20 M; (c) $T = 308$ K, [**1**] = 0.01 M, [**4**] = 0.60 M; (d) $T = 308$ K, [**1**] = 0.01 M, [**4**] = 0.60 M. Solid lines in (a) and (b) correspond to the best nonlinear fitting (see text).

This indicates that the isomerization of complex **7** to **9** (and its consequent coupling to **5** plus Pd^0) is, comparatively, a less important transformation during the catalyzed experiments.

Monitoring the Transmetalation and Isomerization Reactions. The possible participation of two different catalysts (**1** and **2**) in the coupling studied gives rise to a kinetically complicated system, where the catalytic pathways are not only doubled but also interconnected (Scheme 3). For instance, *cis*-[PdRfI(PPh_3)$_2$] (**2**) is being observed during the catalysis, under continuous formation, by oxidative addition of RfI and continuous consumption, either by its spontaneous isomerization to **1** followed by transmetalation or by direct transmetalation. A kinetic study using data from the

Scheme 4



catalytic process is complicated, due to the fact that the system is continuously being refueled with **2** by effect of the oxidation of PdL_2 with the electrophile **3**. In order to simplify the study, this refueling step can be disconnected by simply frustrating the recycling at the oxidative addition step. This means we need to study separately the noncyclic processes of transmetalation plus coupling.

The absence or presence of RfI (**3**) in solution is not expected to exert any influence on the rate constants of the other steps of the cycle. Since both catalysts **1** and **2** (the species on which the transmetalation takes place) are isolable, rate constants for Scheme 3 can be determined in the studies starting at the transmetalation step, assuming that the reductive elimination takes place on **9** and is very fast and irreversible and the oxidative addition is faster than the transmetalation step. Thus, it is assumed that the rate at which the undetected **9** is formed corresponds to the rate at which **5** is formed. These studies, starting from **1** or **2**, are shown in Figure 3 and were carried out under two different conditions: (a) and (b) at 323 K, with catalyst:PhC_2SnBu_3 = 1:20 (as in the previous catalyses); and (c) and (d) at 308 K, with catalyst:PhC_2SnBu_3 = 1:60.

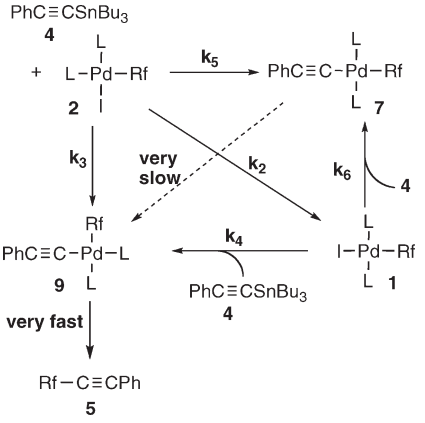
The reaction profiles using **1** were very simple and showed that the isomerization to give **2** is negligible (only **1** was observed), as expected from the very different thermodynamic stabilities of the complexes. Complexes **7** and **9** were formed competitively at very similar rates, and the corresponding rate constants ($k_4 = 6.6 \times 10^{-5}$ M s^{-1} and $k_6 = 7.6 \times 10^{-5}$ M s^{-1}) were obtained (Scheme 4).[27] Since the isomerization of **7** to **9** is very slow under the reaction conditions, all the initial formation of **9** observed in Figure 3a,c can be correctly assigned to direct transmetalation on **1**. In other words, **7** and **9** are formed from **1** by transmetalation at very similar rates.

The profile of the transmetalation on complex **2** was more complicated (Figure 3 b,d). It can be seen at 323 K that **2** isomerizes to **1** quite rapidly. At the same time, **7** and **5** start to be formed, and it is difficult to tell whether they are formed in part from **2**. At lower temperatures (308 K) the initial rate of formation of **5** suggests that, in part, it proceeds from transmetalation on **2**. Hence, the conversions shown in Scheme 5 need to be considered.

A parallel experiment of isomerization of **2** to **1**, under the same conditions of solvent, concentration, and temperature, but without organotin reagent, afforded a value for the isomerization rate constant of $k_2 = 2.7 \times 10^{-4}$ s^{-1}, and it could be seen that this rate did not change significantly in the

(27) Small variations of the observed isomerization rate constant depending on the conditions are due to self-dissociation of PPh_3. See ref 21 for mechanistic details.

Scheme 5



presence of **3**.[28] When this k_2 value and the previously determined k_4 and k_6 values were applied to the system in Scheme 5, the values of k_3 and k_5 could be determined.[29] The fittings of the concentration/time experimental data of the transmetalation/isomerization experiments were made using a nonlinear least-squares fitting program, assuming that the transmetalation is the rate-limiting step and taking into account the isomerization of **2** to **1**, as well as the unproductive transmetalation to give **7**.[30]

The results are summarized in Table 1, which shows that (i) the rates of transmetalation on **1** and **2** are very similar; (ii) either complex leads to **7** and **9** at not very different rates; (iii) however, each complex shows a small preference toward retention of its configuration ($k_3 > k_5$ and $k_6 > k_4$); (iv) k_3 is comparable to k_2 ($k_2/k_3 = 2.73$), meaning that, under catalytic conditions with a large excess of the organotin reagent, the two processes (transmetalation and isomerization) will compete in rate. Furthermore, according to these values, the cis complex **2** is somewhat more efficient than the trans complex **1** in giving the cis product, thus reducing the detrimental formation of **7**. This effect is more clearly observable when working at lower temperature and higher concentration of organotin (Figure 3c vs Figure 3d).

The same model was used to fit the catalytic experiments, affording the results in Table 2. The rate constants found are somewhat higher than those obtained in the transmetalation experiments. This is because in the catalytic experiments the reductive elimination is immediately followed by oxidative addition, which recycles the palladium and the phosphine formed in the reductive elimination. In contrast, in the transmetalation experiments there is no oxidative addition after the coupling, and the Pd(0) and free PPh_3 released accumulate, providing a changing concentration of free phosphine throughout the experiment and affecting progressively the observed rates. Since this effect could not be corrected, the apparent rate constants calculated in the transmetalation experiments (Table 1) are somewhat

(28) The value obtained is slightly different from the reported data, which has been attributed to the eventual presence of traces of ligand in the slowest system or to the partial oxidation of phosphine in the fastest reaction.[21]

(29) Alternatively, a multivariant experiment fixing only k_2 allows us to obtain the four constants k_4, k_6, k_3, and k_5 for the same experiments. The values obtained are very similar (see the Supporting Information).

(30) The multivariable adjustment program Gepasi was used: Mendes, P. *Comput. Appl. Biosci.* **1993**, *9*, 563–571. See the Supporting Information for additional details.

Table 1. Rate Constants ($\times 10^5$ M^{-1} s^{-1}) for the Different Reactions of the Proposed Mechanism in Schemes 4 and 5 in THF at 323 K,[a] for the Data Obtained from the Transmetalation Reactions

cat.	k_3	k_4	k_5	k_6
trans-[PdRfI(PPh_3)$_2$]		6.6 ± 0.1		7.6 ± 0.1
cis-[PdRfI(PPh_3)$_2$]	9.9 ± 0.4	6.6[b]	2.9 ± 0.4	7.6[b]

[a] The errors are given as standard deviations. [b] This rate constant has been fixed for the nonlinear least-squares fitting.

Table 2. Rate Constants ($\times 10^4$ M^{-1} s^{-1}) for the Different Reactions of the Proposed Mechanism in Scheme 3 in THF at 50 °C,[a,b] for the Data Obtained from the Catalytic Reactions[c]

cat.	k_3	k_4	k_5	k_6
trans-[PdRfI(PPh_3)$_2$]	1.4 ± 0.9	5.5 ± 0.2	0.3 ± 0.9	2.7 ± 0.2
cis-[PdRfI(PPh_3)$_2$]	4.6 ± 0.2	4.6 ± 0.1	1.7 ± 0.2	1.6 ± 0.1

[a] See the Supporting Information for additional details. [b] Errors are given as standard deviations. [c] k_2 has been fixed to its known value. The reductive elimination and the oxidative addition have been assumed to be much faster than the transmetalation steps.

underestimated, and those in Table 2, not affected by the problem, are better.

Conclusions

Real systems are far more complex than the simple image of the metal-catalyzed cycles that is cursorily assumed. Depending on the specific combination of reagents and ligands, different alternative pathways can become accessible or dominant. In the case studied here, each of the two products of the oxidative addition becomes the subject of the transmetalation step. This happens because of the slow isomerization of the initial *cis*-[PdRfI(PPh_3)$_2$] into the most stable *trans*-[PdRfI(PPh_3)$_2$]. Later, *cis*-[PdRf(C≡CPh)(PPh_3)$_2$] and *trans*-[PdRf(C≡CPh)(PPh_3)$_2$] are competitively formed and, because of the very slow isomerization of the later into *cis*-[PdRf(C≡CPh)(PPh_3)$_2$] (which is the only gate to the coupling product), the coupling reaction is partially frustrated by accumulating this relatively inert intermediate.

It is also worth noting that in the early stages of the studies of the Stille reaction it was assumed that the transmetalation step was rate-determining (rds).[31] Later we could show that also the oxidative addition or the reductive elimination can happen to be the rds.[6,4] Here we have found that the usually ignored isomerization steps, which are hardly shown in the cycles, are extremely important and can block or allow a reaction pathway, which is decisive in the success or frustration of the chemical transformation pursued.

Experimental Section

General Methods. All reactions were carried out under N_2 or Ar in THF dried using a Solvent Purification System (SPS). NMR spectra were recorded on Bruker ARX 300 and AV 400 instruments equipped with a VT-100 variable-temperature probe. Chemical shifts are reported in ppm from tetramethylsilane (^{1}H), CCl_3F (^{19}F), and 85% H_3PO_4 (^{31}P), with positive shifts downfield, at ambient probe temperature unless otherwise stated. The temperatures for the NMR probe were calibrated using ethylene glycol as a temperature standard.[32] In the ^{19}F or ^{31}P NMR spectra measured in nondeuterated solvents, a coaxial tube containing acetone-d_6 was used to maintain the lock ^{2}H signal. Combustion CHN analyses were made on a Perkin-Elmer 2400 CHN microanalyzer. The compounds [Pd(PPh_3)$_4$],[33] *trans*-[PdRf$_2$(tht)$_2$],[34] [Pd$_2$($C_6Cl_2F_3$)$_2$(μ-Cl)$_2$(tht)$_2$],[13] *trans*-[Pd($C_6Cl_2F_3$)Cl(PPh_3)$_2$],[6] *trans*-[Pd($C_6Cl_2F_3$)I(PPh_3)$_2$] (**1**),[6] *cis*-[Pd($C_6Cl_2F_3$)I(PPh_3)$_2$] (**2**),[21] $C_6Cl_2F_3I$ (**3**),[21] and *trans*-[Pd($C_6Cl_2F_3$)(OTf)(PPh_3)$_2$][5] were prepared by literature methods.

Synthesis. $C_6Cl_2F_3C$≡CPh (5). To a stirred solution of [Pd($C_6Cl_2F_2$)I($AsPh_3$)$_2$] (62.7 mg; 0.060 mmol) and $C_6Cl_2F_3I$ (**3**) (392 mg; 1.20 mmol) in THF (6 mL) was added Sn(C≡CPh)Bu_3 (**4**) (420.6 mL; 1.20 mmol). The solution was heated under reflux for 48 h. Then, the mixture was evaporated to dryness. The residue was treated with diethyl ether (10 mL) and a saturated solution of KF (10 mL). The mixture was stirred vigorously, and then $SnFBu_3$ was separated by filtration. The solution was dried over $MgSO_4$ and evaporated to crystallize the desired product (yield 217 mg, 60%). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 157.4 (dm, $^1J_{C-F}$ = 255.3 Hz, *o*-*C*F), 155.0 (dm, $^1J_{C-F}$ = 254.1 Hz, *p*-*C*F), 132.1 (s, *o*-*C*H), 129.8 (s, *p*-*C*H), 128.7 (s, *m*-*C*H), 121.9 (s, *C*Ph), 107.7 (t, $^2J_{C-F}$ = 21.7 Hz, *C*$C_6Cl_2F_3$), 101.2 (s, *C*≡C), 73.8 (s, *C*≡C). ^{19}F NMR ($CDCl_3$/THF 293 K): δ −108.86/−109.55 (d, $^4J_{F-F}$ = 1.9 Hz, *o*-C*F*), −110.21/−110.72 (t, $^4J_{F-F}$ = 1.9 Hz, *p*-C*F*). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.62−7.57 (m, Ph), 7.43−7.39 (m, Ph). Anal. Calcd for $C_{14}H_5Cl_2F_3$ (mol wt 301.097): C, 55.85; H, 1.67. Found: C, 55.90; H, 1.92.

***trans*-[Pd($C_6Cl_2F_3$)(C≡CPh)(PPh_3)$_2$ (7).** *trans*-[Pd($C_6Cl_2F_3$)(OTf)(PPh_3)$_2$] (500 mg, 0.501 mmol) and PPh_3 (272 mg, 1.04 mmol) were dissolved in THF (25 mL). The organotin compound PhC≡C$SnBu_3$ was then added via syringe at 0 °C. The solution was stirred until it turned deep brown (15 h). Then, the mixture was evaporated to dryness. The residue was extracted in THF/EtOH and evaporated again. The solid was washed with EtOH and vacuum-dried. The solid residue was recrystallized from CH_2Cl_2/EtOH at −28 °C (yield 230 mg, 39%). ^{19}F NMR ($CDCl_3$/THF): δ −90.90/−90.02 (t), −122.40/−122.49 (s). ^{31}P NMR (THF): δ 28.03. Anal. Calcd for $C_{50}H_{35}Cl_2F_3P_2Pd$: C, 64.43; H, 3.78. Found: C, 63.76; H, 3.61.

General Procedure for Kinetic Study. The kinetic experiments were monitored by ^{19}F NMR. In a standard experiment of catalysis, an NMR tube graduated to 0.5 mL was charged with the palladium complex **1** or **2** (5×10^{-3} mmol) and $C_6Cl_2F_3I$ (**3**) (0.1 mmol) and dissolved under Ar or N_2 at room temperature in THF (~0.3 mL). Then, the NMR tube was cooled to −78 °C, PhC≡C$SnBu_3$ (**4**; 0.1 mmol) was added, and further THF was added to reach the 0.50 mL mark. The NMR tube was charged with an acetone-d_6 capillary for NMR lock and placed into a thermostated probe (323.0 ± 0.2 K).

In a standard experiment of transmetalation, an NMR tube was charged with the palladium complex **1** or **2** (5×10^{-3} mmol) and dissolved under Ar at room temperature in THF (~0.3 mL). Then, the NMR tube was cooled to −78 °C, PhC≡C$SnBu_3$ (**4**; 0.1 mmol) was added, and further THF was added to reach 0.50 mL final volume. The NMR tube was charged with an acetone-d_6 capillary for NMR lock and placed into a thermostated probe (323.0 ± 0.2 or 308 ± 0.2 K). The kinetic experiments were monitored by ^{19}F NMR, and concentration−time data were acquired by integration of the ^{19}F NMR signals. The fluorine integrals of the ^{19}F NMR were corrected to compensate the different relaxation times of the nuclei in different substances. This was done by measuring the integral of samples containing mixtures of accurately weighed amounts of RfI or RfCCPh with (fluoroaryl)palladium complexes and adjusting the value of the integrals to the calculated (from their weight) values. The same

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ratio was used to multiply the integrals in the kinetic experiments.

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Supporting Information Available: Text, figures, and tables giving kinetic data and details of the kinetic analysis. This material is available free of charge via the Internet at http://pubs.acs.org.