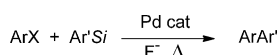


# Three Roles for the Fluoride Ion in Palladium-Catalyzed Hiyama Reactions: Transmetalation of $[\text{ArPdFL}_2]$ by $\text{Ar}'\text{Si}(\text{OR})_3$ \*\*

Christian Amatore,\* Laurence Grimaud,\* Gaëtan Le Duc, and Anny Jutand\*

**Abstract:** From the kinetic data on the transmetalation/reductive elimination in fluoride-promoted Hiyama reactions, obtained using electrochemical techniques, it has been established that fluoride ions play three roles.  $\text{F}^-$  reacts with  $\text{trans}[\text{ArPdBrL}_2]$  ( $\text{L} = \text{PPh}_3$ ) to form  $\text{trans}[\text{ArPdFL}_2]$ , which reacts with  $\text{Ar}'\text{Si}(\text{OMe})_3$  in the rate-determining transmetalation, whereas  $\text{trans}[\text{ArPdBrL}_2]$  does not react with  $\text{Ar}'\text{Si}(\text{OMe})_3$ .  $\text{F}^-$  reacts with  $\text{Ar}'\text{Si}(\text{OMe})_3$  to deliver the unreactive silicate  $\text{Ar}'\text{SiF}(\text{OMe})_3^-$ , thus leading to two antagonistic kinetic effects. In addition,  $\text{F}^-$  catalyzes the reductive elimination from intermediate  $\text{trans}[\text{ArPdAr}'\text{L}_2]$ .

The palladium-catalyzed Hiyama reactions between arylhalides and arylsilanes  $\text{Ar}'\text{Si}[\text{Si} = \text{Si}(\text{OR})_3, \text{SiRF}_2, \text{SiF}_3]$  are promoted by fluoride ions. They are often performed at high temperatures even with aryl iodides (Scheme 1).<sup>[1,2]</sup>



**Scheme 1.** Hiyama reactions promoted by fluoride ions.

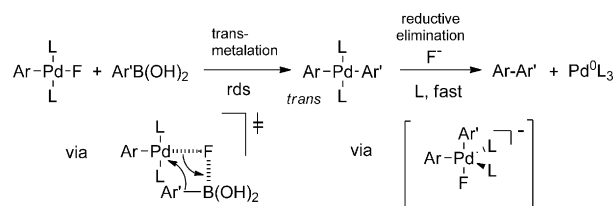
The postulated mechanism of the Hiyama reaction involving  $\text{Ar}'\text{SiRF}_2$  predicted a transmetalation of  $[\text{ArPdXL}_2]$  (formed in the oxidative addition of  $\text{ArX}$  to  $[\text{Pd}^0\text{L}_4]$ ) with the silicate  $\text{Ar}'\text{SiRF}_3^-$ , thus leading to  $[\text{ArPdAr}'\text{L}_2]$  which generates  $\text{ArAr}'$  and  $[\text{Pd}^0\text{L}_2]$ .<sup>[2a]</sup> A transition state involving a Pd–F bond was also proposed.<sup>[2b]</sup> DFT calculations on the model reaction of  $\text{CH}_2=\text{CH}-\text{I}$  with  $\text{CH}_2=\text{CH}-\text{SiMe}_3$  in the presence of  $\text{F}^-$  ruled out the participation of a silicate in the transmetalation. They predicted I–F exchange in  $\text{CH}_2=\text{CH}-[\text{PdIL}_2]$  ( $\text{L} = \text{PMe}_3$ ) to give  $\text{CH}_2=\text{CH}-[\text{PdFL}_2]$ . A coordination of the C=C bond of  $\text{CH}_2=\text{CH}-\text{SiMe}_3$  to the palladium(II) center led to  $\text{CH}_2=\text{CH}-[\text{PdF}(\eta^2\text{-CH}=\text{CH}-\text{SiMe}_3)\text{L}]$ .<sup>[2c]</sup> The transmetalation would then occur from the latter in an unimolecular process. A nucleophilic attack of  $\text{F}^-$  onto the Si center of the coordinated  $\text{CH}=\text{CH}-\text{SiMe}_3$  in  $\text{CH}_2=\text{CH}-[\text{PdI}(\eta^2\text{-CH}=\text{CH}-\text{SiMe}_3)\text{L}]$  favoring the intramolecular transmetalation was also examined. Those two pathways are

quite unlikely with  $\text{Ar}'\text{Si}(\text{OR})_3$  reagents because of the improbable coordination of the latter onto a palladium(II) center. A mechanism has been proposed for the reaction of the silanols  $\text{RSi}(\text{OH})\text{Me}_2$  with  $\text{ArI}$ , promoted by  $\text{F}^-$ , in which a first-order dependence was found for  $\text{F}^-$  at low concentrations and an inverse-order reaction at high concentrations. The authors proposed two different pathways towards the fluoride-activated disiloxane  $[\text{RSi}(\text{Me})_2(\text{F})\text{OSi}(\text{Me})_2\text{R}]^-$  which is involved in a transmetalation with  $[\text{ArPdI}]$ .<sup>[3b]</sup>

We recently established that fluoride ions are involved in two kinetically antagonistic effects in Suzuki–Miyaura reactions:  $\text{F}^-$  is required to generate  $\text{trans}[\text{ArPdFL}_2]$  [Eq. (1)]



which reacts with  $\text{Ar}'\text{B}(\text{OH})_2$  in the rate-determining transmetalation (Scheme 2).<sup>[4a]</sup> However, at too high a concentration,  $\text{F}^-$  inhibits the reaction by competitive formation of the unreactive  $\text{Ar}'\text{B}(\text{OH})_{3-n}\text{F}_n^-$  ( $n = 1-3$ ). Moreover,  $\text{F}^-$  pro-



**Scheme 2.** Mechanism of the transmetalation/reductive elimination in the Suzuki–Miyaura reaction performed in the presence of  $n\text{Bu}_4\text{NF}$ .<sup>[4]</sup> rds = rate-determining step.

motes the reductive elimination from  $\text{trans}[\text{ArPdAr}'\text{L}_2]$ , thus making this reaction faster than the transmetalation, which becomes rate determining (Scheme 2). The rate of the overall reaction performed with  $\text{trans}[\text{ArPdXL}_2]$  is thus controlled by the  $[\text{F}^-]/[\text{Ar}'\text{B}(\text{OH})_2]$  ratio.<sup>[4]</sup>

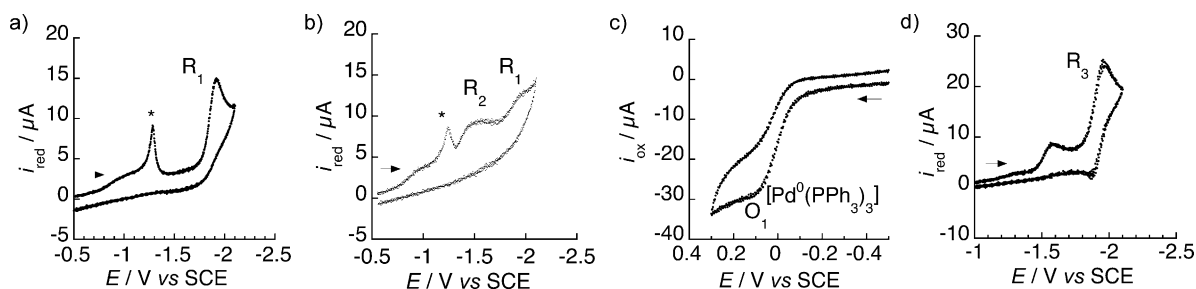
We report herein the kinetic and mechanistic data aimed to understand the role of fluoride anions in Hiyama reactions performed with  $\text{PhSi}(\text{OMe})_3$  (**1**). Three roles for  $\text{F}^-$  were discovered, including the transmetalation of  $[\text{ArPdF}(\text{PPh}_3)_2]$  with  $\text{Ar}'\text{Si}(\text{OMe})_3$ .

Fluoride ions react with  $\text{trans}[\text{ArPdX}(\text{PPh}_3)_2]$ <sup>[4a]</sup> to form  $\text{trans}[\text{ArPdF}(\text{PPh}_3)_2]$  [Eq. (1)].<sup>[4a,5]</sup> The isolated  $\text{trans}[\text{p-CNC}_6\text{H}_4\text{-Pd-F}(\text{PPh}_3)_2]$  (**2**)<sup>[4a]</sup> ( $C_0 = 2 \text{ mM}$ ) was first submitted to a reaction with  $\text{PhSi}(\text{OMe})_3$  (**1**) in DMF at  $25^\circ\text{C}$ . The reaction was performed in the presence of  $\text{PPh}_3$  (2 equiv) to afford the stable and thus detectable  $[\text{Pd}^0(\text{PPh}_3)_3]$  (**5**). The reaction was monitored by cyclic voltammetry (CV). The reduction peak  $R_1$  of **2** ( $E_{R1}^0 = -1.95 \text{ V vs SCE}$ , Figure 1a), whose peak current was proportional to its concentration,

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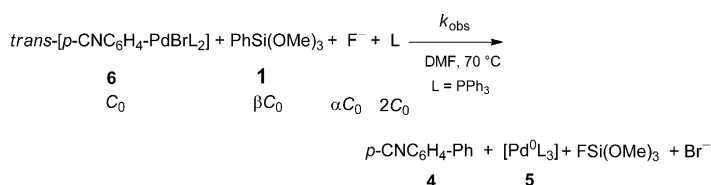
**Figure 1.** Cyclic voltammetry performed in DMF containing  $n\text{Bu}_4\text{NBF}_4$  (0.3 M) in the presence of  $\text{PPh}_3$  (4 mM) at a gold disk electrode ( $d=2$  mm) at the scan rate of  $0.5\text{ V s}^{-1}$ , at  $25^\circ\text{C}$ . a) Reduction at  $R_1$  of  $\text{trans-[p-CNC}_6\text{H}_4\text{-Pd-F(PPh}_3)_2]$  (**2**) (2 mM). b) 30 min after addition of  $\text{PhSi(OMe)}_3$  (**1**;  $\beta=30$  equiv versus **2**) to **2**: reduction of  $\text{trans-[p-CNC}_6\text{H}_4\text{-Pd-Ph(PPh}_3)_2]$  (**3**) at  $R_2$ . c) Oxidation at  $O_1$  of  $[\text{Pd}^0(\text{PPh}_3)_3]$  (**5**) formed after addition of  $\text{F}^-$  ( $\alpha=40$  equiv versus **2**) to **3** after 20 min. d) Reduction at  $R_3$  of  $p\text{-CNC}_6\text{H}_4\text{-Ph}$  (**4**) formed together with **5** under the reaction conditions described for Figure 1 c after 22 min. \* = Adsorption peak.

progressively disappeared in the presence of **1** ( $[\text{I}]=\beta C_0$ ,  $\beta=30$  equiv), thus leading to the intermediate palladium(II) complex  $\text{trans-[p-CNC}_6\text{H}_4\text{-Pd-Ph(PPh}_3)_2]$  (**3**) characterized by its reduction peak  $R_2$  ( $E_{R_2}^p=-1.47\text{ V vs SCE}$ ) (Figure 1 b). The same complex was formed in our previous work when **2** was reacted with  $\text{PhB(OH)}_2$ .<sup>[4,6]</sup> However, the reaction of **2** with **1** was much slower than that of  $\text{PhB(OH)}_2$  at identical concentrations.<sup>[4]</sup> It is only after addition of  $n\text{Bu}_4\text{NF}$  ( $[\text{F}^-]=\alpha C_0$ ,  $\alpha=40$  equiv, from a stock solution 1 M in THF) that the intermediate complex **3** disappeared and the solution turned to yellow, thus leading to  $p\text{-CNC}_6\text{H}_4\text{Ph}$  (**4**) (99%) and  $[\text{Pd}^0(\text{PPh}_3)_3]$  (**5**) (96%). The compound **4** was characterized by its reduction peak at  $-2.0\text{ V}$  ( $R_3$ , reversible) and **5** by its oxidation peak at  $+0.05\text{ V}$  ( $O_1$ ) (Figures 1 c,d). Their yield was determined from the increase of their respective current after addition of a known amount of the authentic samples **4** and **5**.

These results establish for the first time that  $\text{trans-[ArPdFL}_2]$  undergoes transmetalation with **1** at  $25^\circ\text{C}$  as a consequence of the fluorophilicity of the silicon atom (Scheme 3). Moreover, as already proved in our previous work,  $\text{F}^-$  ions promote the reductive elimination from the stable  $\text{trans-[ArPdAr'L}_2]$  (Scheme 3).<sup>[4,7]</sup>

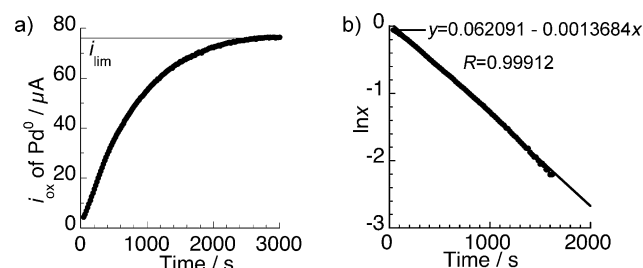
In contrast to **2**, the cyclic voltammetry showed that  $\text{trans-[p-CNC}_6\text{H}_4\text{-Pd-Br(PPh}_3)_2]$  (**6**;  $C_0=2\text{ mM}$  in DMF, characterized by its reduction peak at  $-1.83\text{ V vs SCE}$ ) did not react with **1** (from  $\beta=10$  to 50 equiv versus **6**) in the presence of 2 equivalents of  $\text{PPh}_3$  at  $25^\circ\text{C}$ . The compounds **4** and **5** were not formed in the presence of  $\text{F}^-$  ( $\alpha=25$  equiv versus **6** for  $\beta=30$ ) at room temperature (see below). Conversely, a reaction took place at  $70^\circ\text{C}$  and it delivered the cross-coupling

product **4** as well as **5**. The role of  $\text{F}^-$  in the reaction shown in Scheme 4 could thus be investigated. With four  $\text{PPh}_3$  units per palladium center, those reaction conditions mimicked a Hiyama reaction catalyzed by  $[\text{Pd}^0(\text{PPh}_3)_4]$ .<sup>[1]</sup>

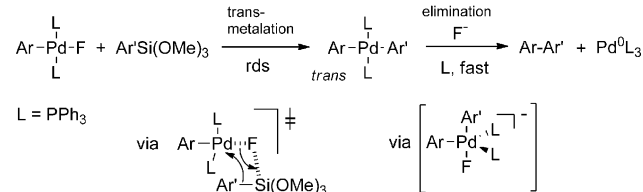


**Scheme 4.** Model reaction.

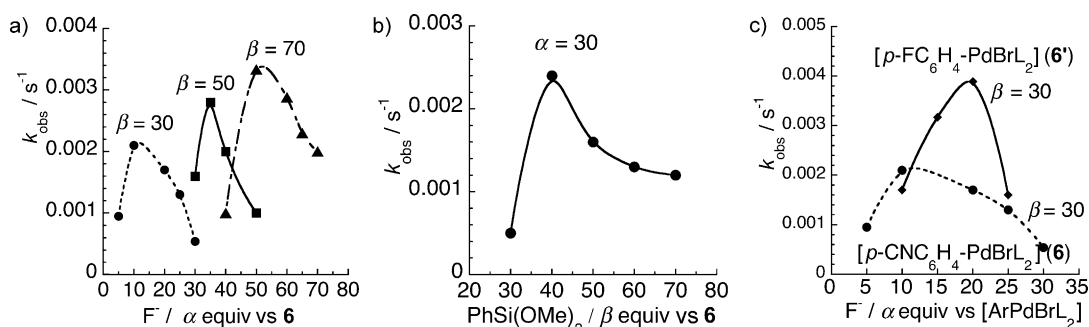
The kinetics of the formation of **5** was monitored by chronoamperometry at a rotating gold disk electrode polarized at  $+0.1\text{ V}$  (oxidation potential of **5** in DMF). The increase of the oxidation current of **5** (proportional to its concentration) was recorded with time just after addition of  $n\text{Bu}_4\text{NF}$  ( $\alpha=25$  equiv) to a solution containing **6** ( $C_0=2\text{ mM}$ ), **1** ( $\beta=30$  equiv), and  $\text{PPh}_3$  (2 equiv) at  $70^\circ\text{C}$  (Figure 2 a). The plot of  $\ln x$  versus time was linear (Figure 2 b;  $x=(i_{\text{lim}}-i_t)/i_{\text{lim}}$  where  $i_{\text{lim}}$ =final oxidation current of **5**;  $i_t$ =oxidation current of **5** at time  $t$ ). The value of  $k_{\text{obs}}$ ,  $1.4 \times 10^{-3}\text{ s}^{-1}$  (DMF,  $70^\circ\text{C}$ ), was determined from the slope of the linear correlation (Figure 2 b). At the end of the reaction, **5** and **4** were formed



**Figure 2.** Kinetics of the reaction of  $\text{trans-[p-CNC}_6\text{H}_4\text{-Pd-Br(PPh}_3)_2]$  (**6**;  $C_0=2\text{ mM}$ ) with **1** ( $\beta=30$  equiv versus **6**) in the presence of  $\text{PPh}_3$  (2 equiv) and  $n\text{Bu}_4\text{NF}$  ( $\alpha=25$  equiv versus **6**) in DMF at  $70^\circ\text{C}$ . a) Evolution of the oxidation current of **5** (proportional to its concentration) measured by chronoamperometry at a rotating gold disk electrode ( $d=2$  mm) polarized at  $+0.1\text{ V vs SCE}$ . b) Variation of  $\ln x$  versus time (see text for the definition of  $x$ ).



**Scheme 3.** Mechanisms of the transmetalation/reductive elimination in the presence of  $\text{F}^-$ .



**Figure 3.** Reaction of **6** (2 mM) with **1** in the presence of  $F^-$  ( $\alpha$  equiv versus **6**) and  $PPh_3$  (2 equiv) in DMF at 70°C. a) Plot of the pseudo-first-order rate constant  $k_{obs}$  versus  $F^-$  ( $\alpha$  equiv versus **6**) in the presence of **1** ( $\beta = 30, 50$  and 70 equiv versus **6**). b) Plot of  $k_{obs}$  versus **1** ( $\beta$  equiv versus **6**) in the presence of  $F^-$  ( $\alpha = 30$  equiv versus **6**). c) Plot of  $k_{obs}$  vs  $F^-$  ( $\alpha$  equiv) for the reaction of **1** ( $\beta = 30$  equiv) with **6** and *trans*-[ $p\text{-FC}_6\text{H}_4\text{-Pd-Br(PPh}_3)_2$ ] **6'**.

in 97 and 98% yield respectively (see Figure S1a,b in the Supporting Information).

The plots of  $k_{obs}$  versus  $F^-$  concentration ( $\alpha$  equiv versus **6**) exhibited a maximum regardless of the concentration of **1** (Figure 3a). The dependence of  $k_{obs}$  versus the concentrations of  $F^-$  and **1** revealed that  $k_{obs}$  characterized the rate of the transmetalation, which was rate-determining, with a subsequent faster reductive elimination. The plot of  $k_{obs}$  versus the concentration of **1** at constant  $F^-$  concentration also exhibited a maximum (Figure 3b). The fluoride was required to let the transmetalation proceed, but the reaction became slower when the concentration of **1** was too high and greatly exceeded that of  $F^-$  (Figure 3b). This result means that at an excess of **1**,  $F^-$  is quenched by **1** to form an unreactive species, the aryl silicate  $[\text{PhSiF(OMe)}_3]^-$  [Eq. (2)]. The affinity of  $F^-$  for silicon centers is indeed well known.<sup>[8]</sup>

Therefore, the bell-shaped curves of Figure 3a,b indicate that fluoride ions led to two kinetically antagonistic effects because  $F^-$  is involved in two competitive equilibria (Scheme 5): one delivers the reactive *trans*-[ $\text{ArPdF(PPh}_3)_2$ ] which reacts with  $\text{Ar'Si(OMe)}_3$  in the rate-determining transmetalation; the second one delivers the unreactive silicate  $\text{Ar'SiF(OMe)}_3^-$ . As for the Suzuki–Miyaura reaction,<sup>[4a]</sup> for  $\beta > 30$  the maximum value of  $k_{obs}$  under each of the reaction conditions was observed for  $\alpha/\beta = [F^-]/[\text{PhSi(OMe)}_3]$  values in the range 0.7–0.8, that is, less than unity (see Figure S2 in the Supporting Information). A bell-shaped plot of  $k_{obs}$  versus  $F^-$  concentration was also observed for another complex **6'**

though with different  $\alpha$  values for the same  $\beta$  value (Figure 3c).

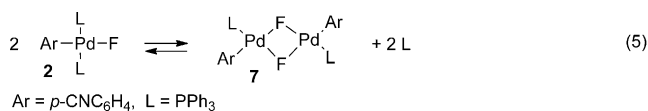
The kinetic laws for the mechanism in Scheme 5 are expressed in Equations (3) and (4).<sup>[9]</sup>

$$\text{rate} = k_{obs} [\text{Pd}^{\text{II}}]_{\text{total}} \quad (3)$$

$$k_{obs} = k_{tm} \beta C_0 \left( \frac{1}{1 + K_F [F^-]} \right) \left( \frac{K_X [F^-]}{[X^-] + K_X [F^-]} \right) \quad (4)$$

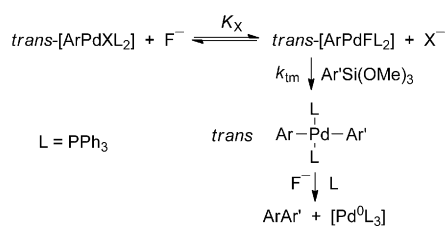
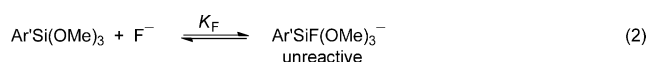
When  $[F^-] \ll 1/K_F$  and  $[F^-] \ll C_0/(2K_X)$ , then  $k_{obs} \rightarrow 2k_{tm}\beta K_X [F^-]$ , and  $k_{obs}$  increases linearly with  $[F^-]$  at low concentrations. Conversely, when  $[F^-] \gg 1/K_F$  and  $[F^-] \gg C_0/(2K_X)$ , then  $k_{obs} \rightarrow k_{tm}\beta C_0/(K_F [F^-])$  and  $k_{obs}$  decreases hyperbolically with  $[F^-]$  at high concentrations of  $[F^-]$ . The theoretical variation of  $k_{obs}$  versus  $[F^-]$  passes through a maximum, and is in agreement with the experimental observations (Figure 3a).

As stated above, the reaction in Scheme 4 did not work at 25°C regardless of the  $\alpha/\beta$  ratio (0.5, 0.75). Neither **5** nor  $\text{ArAr'}$  were formed. However, another reaction took place, thus affording the new complex **7**, which is characterized by



its reduction peak at  $-2.17$  V (see Figure S3 in the Supporting Information). The addition of  $F^-$  ( $\alpha = 5$  equiv) to **6** (2 mM) partly generated **2** [Eq. (1)]. This step was clearly observed by CV where the reduction peaks  $R_1$  and  $R_2$  of **2** and **6**, respectively, coexisted. Both disappeared ultimately in the absence or presence of **1**, thus leading to the new complex **7**. The  $^{31}\text{P}$  NMR analysis of the solutions exhibited a major singlet at  $\delta = 31.77$  ppm as is observed for the dimer **7** which is generated by reacting  $[\text{p-CNC}_6\text{H}_4\text{-Pd}(\mu\text{-I})(\text{PPh}_3)_2]$  with  $n\text{Bu}_4\text{NF}$  (20 equiv) (see Figure S4 in the Supporting Information).<sup>[4a,5]</sup>

The compound **7** was not formed when the isolated **2** was reacted with **1** in the presence of  $\text{PPh}_3$  (2 equiv) at room temperature (see Scheme 3). But it was formed from **6** in the presence of  $F^-$ , **1**, and  $\text{PPh}_3$  (2 equiv) at room temperature.



**Scheme 5.** Mechanisms for the transmetalation with subsequent reductive elimination promoted by fluoride ions.

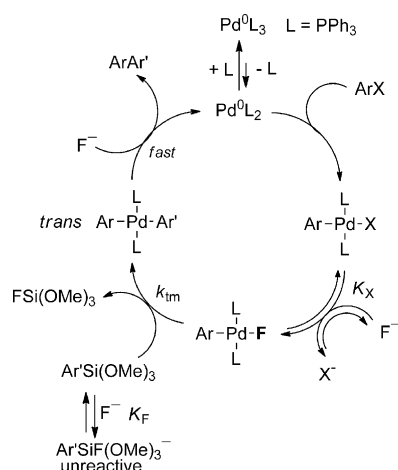
This difference presumably derives from the low thermodynamic concentration of  $[\text{ArPdF}(\text{PPh}_3)_2]$ , when starting from **6**, which did not allow a fast transmetalation and thus, all the aryl/ $\text{Pd}^{\text{II}}$  were converted into the unreactive dimer **7** [Eq. (5)]. Upon increasing the temperature, the reaction of **1** with  $[\text{ArPdF}(\text{PPh}_3)_2]$ , thus leading to  $\text{ArAr}'$  and **5**, became faster and the formation of **7** in Equation (5) was by-passed.

Two other putative pathways have been ruled out. When the preformed silicate  $[\text{PhSiF}(\text{OMe})_3]^-$  (10 equiv) was added to a solution of **6** (2 mM) and  $\text{PPh}_3$  (2 equiv) at 25°C, **6** disappeared, but neither  $\text{ArAr}'$  nor **5** were formed. Only the dimer **7** was detected by its reduction peak at  $-2.17$  V. Consequently, the silicate  $[\text{PhSiF}(\text{OMe})_3]^-$  did not react with **6** at 25°C. However, the formation of **7** attested that some transient  $[\text{ArPdF}(\text{PPh}_3)_2]$  was generated (experimentally observed; see the Supporting Information) by the reaction of **6** with  $\text{F}^-$  [Eq. (1)], the latter being released from  $[\text{PhSiF}(\text{OMe})_3]^-$  in its equilibrium with **1** [Eq. (2)]. This evidence suggests that the affinity of **6** for  $\text{F}^-$  is higher than that of **1** at comparable concentrations.

On the other hand, addition of the preformed  $[\text{PhSiF}(\text{OMe})_3]^-$  (10 equiv) to a solution of **2** (2 mM) in the presence of  $\text{PPh}_3$  (2 equiv) at 25°C delivered the coupling product **4** (42%) and **5**, but in a slow reaction (80 min), much slower than that of **1** at the same concentration at 25°C because the reaction proceeded via **1**, which was generated at low thermodynamic concentration in its equilibrium with  $[\text{PhSiF}(\text{OMe})_3]^-$  [Eq. (2)]. This result is in agreement with the slow reactions observed from **6** at high fluoride concentrations where both  $[\text{PhSiF}(\text{OMe})_3]^-$  and **2** were the major species (Figure 3a).

Consequently, the most efficient pathway for the transmetalation is the reaction of  $\text{trans-}[\text{ArPdF}(\text{PPh}_3)_2]$  with  $\text{Ar}'\text{Si}(\text{OMe})_3$ , a reaction which even takes place at room temperature. The three roles of  $\text{F}^-$  in the Hiyama reactions are displayed in Scheme 6.

In conclusion, the three mechanistic roles of fluoride ions in Hiyama reactions involving  $\text{Ar}'\text{Si}(\text{OMe})_3$  have been established. The crucial step is the formation of  $\text{trans-}$



**Scheme 6.** Mechanism of the Hiyama reaction performed in the presence of fluoride anions ( $n\text{Bu}_4\text{NF}$ ) at 70°C.

$[\text{ArPdF}(\text{PPh}_3)_2]$ , which reacts with  $\text{Ar}'\text{Si}(\text{OMe})_3$  in a rate-determining transmetalation step, whereas the silicate  $[\text{Ar}'\text{SiF}(\text{OMe})_3]^-$  is not reactive. This process leads to two antagonistic roles of  $\text{F}^-$  and the rate of the overall reaction is controlled by the ratio  $[\text{F}^-]/[\text{Ar}'\text{Si}(\text{OMe})_3]$ , which must be less than unity. A third role exerted by  $\text{F}^-$  is the promotion of the reductive elimination from  $\text{trans-}[\text{ArPdAr}'(\text{PPh}_3)_2]$ , as was already established in the Suzuki–Miyaura coupling.<sup>[4]</sup> The overall reactions starting from  $\text{trans-}[\text{ArPdBr}(\text{PPh}_3)_2]$  in the Hiyama reactions are much slower than those in Suzuki–Miyaura reactions at the same concentration of reagents and  $\text{F}^-$  since the former do not take place at 25°C. This study explains why arylboronic acids can react with aryl iodides or bromides at room temperature, whereas arylsilanes require higher temperatures.<sup>[1,2]</sup>

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