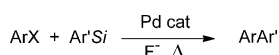


Three Roles for the Fluoride Ion in Palladium-Catalyzed Hiyama Reactions: Transmetalation of $[\text{ArPdFL}_2]$ by $\text{Ar}'\text{Si}(\text{OR})_3$ **

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. 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 $\text{Ar}'\text{Si}(\text{OMe})_3$. 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, 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).^[1,2]



Scheme 1. Hiyama reactions promoted by fluoride ions.

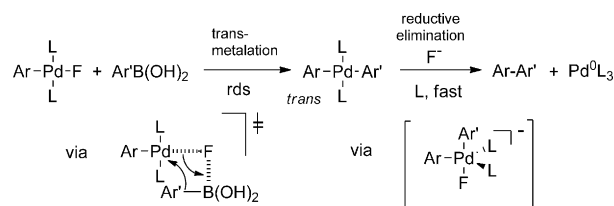
The postulated mechanism of the Hiyama reaction involving $\text{Ar}'\text{SiRF}_2$ predicted a transmetalation of $[\text{ArPdXL}_2]$ (formed in the oxidative addition of ArX to $[\text{Pd}^0\text{L}_4]$) with the silicate $\text{Ar}'\text{SiRF}_3^-$, thus leading to $[\text{ArPdAr}'\text{L}_2]$ which generates ArAr' and $[\text{Pd}^0\text{L}_2]$.^[2a] A transition state involving a Pd–F bond was also proposed.^[2b] 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 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 $\text{CH}_2=\text{CH}-[\text{PdF}(\eta^2\text{-CH}=\text{CH}-\text{SiMe}_3)\text{L}]$.^[2c] The transmetalation would then occur from the latter in an unimolecular process. A nucleophilic attack of 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 ArI , promoted by F^- , in which a first-order dependence was found for 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 $[\text{ArPdI}]$.^[3b]

We recently established that fluoride ions are involved in two kinetically antagonistic effects in Suzuki–Miyaura reactions: 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).^[4a] However, at too high a concentration, 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, F^- pro-



Scheme 2. Mechanism of the transmetalation/reductive elimination in the Suzuki–Miyaura reaction performed in the presence of $n\text{Bu}_4\text{NF}$.^[4] 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.^[4]

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 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 $\text{trans}[\text{ArPdX}(\text{PPh}_3)_2]$ ^[4a] to form $\text{trans}[\text{ArPdF}(\text{PPh}_3)_2]$ [Eq. (1)].^[4a,5] The isolated $\text{trans}[\text{p-CNC}_6\text{H}_4\text{-Pd-F}(\text{PPh}_3)_2]$ (**2**)^[4a] ($C_0 = 2 \text{ mM}$) was first submitted to a reaction with $\text{PhSi}(\text{OMe})_3$ (**1**) in DMF at 25°C . The reaction was performed in the presence of 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,

[*] Dr. C. Amatore, Dr. L. Grimaud, Dr. G. Le Duc, Dr. A. Jutand
Ecole Normale Supérieure-PSL Research University
Département de Chimie, Sorbonne Universités
UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR
24 Rue Lhomond, 75231 Paris Cedex 5 (France)
E-mail: christian.amatore@ens.fr
Anny.jutand@ens.fr

[**] CNRS, ENS, and UPMC are thanked for financial support.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201400956>.

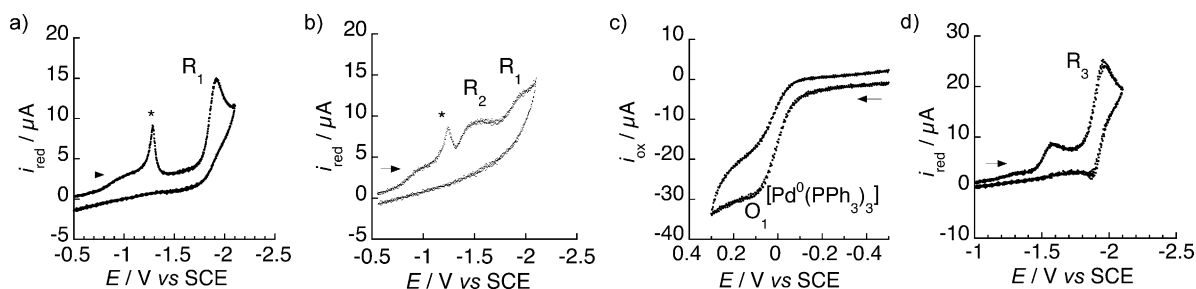


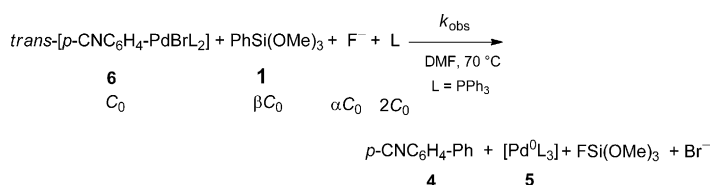
Figure 1. Cyclic voltammetry performed in DMF containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M) in the presence of PPh_3 (4 mM) at a gold disk electrode ($d=2$ mm) at the scan rate of 0.5 V s^{-1} , at 25°C . a) Reduction at R_1 of $\text{trans-[p-CNC}_6\text{H}_4\text{-Pd-F(PPh}_3)_2]$ (**2**) (2 mM). b) 30 min after addition of PhSi(OMe)_3 (**1**; $\beta=30$ equiv versus **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 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 ($E_{\text{P}R_2} = -1.47 \text{ V vs SCE}$) (Figure 1 b). The same complex was formed in our previous work when **2** was reacted with PhB(OH)_2 .^[4,6] However, the reaction of **2** with **1** was much slower than that of PhB(OH)_2 at identical concentrations.^[4] 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 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°C as a consequence of the fluorophilicity of the silicon atom (Scheme 3). Moreover, as already proved in our previous work, F^- ions promote the reductive elimination from the stable $\text{trans-[ArPdAr'L}_2]$ (Scheme 3).^[4,7]

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 V vs SCE) did not react with **1** (from $\beta = 10$ to 50 equiv versus **6**) in the presence of 2 equivalents of PPh_3 at 25°C . The compounds **4** and **5** were not formed in the presence of F^- ($\alpha = 25$ equiv versus **6** for $\beta = 30$) at room temperature (see below). Conversely, a reaction took place at 70°C and it delivered the cross-coupling

product **4** as well as **5**. The role of F^- in the reaction shown in Scheme 4 could thus be investigated. With four PPh_3 units per palladium center, those reaction conditions mimicked a Hiyama reaction catalyzed by $[\text{Pd}^0(\text{PPh}_3)_4]$.^[1]



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 PPh_3 (2 equiv) at 70°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_{lim} = final oxidation current of **5**; i_t = oxidation current of **5** at time t). The value of k_{obs} , $1.4 \times 10^{-3} \text{ s}^{-1}$ (DMF, 70°C), was determined from the slope of the linear correlation (Figure 2 b). At the end of the reaction, **5** and **4** were formed

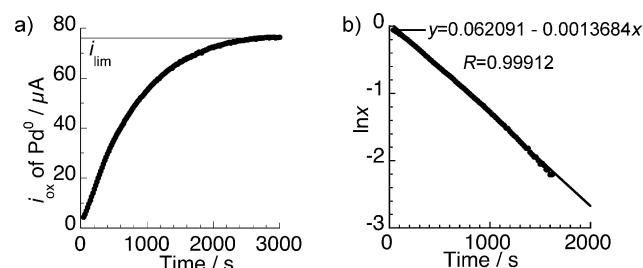
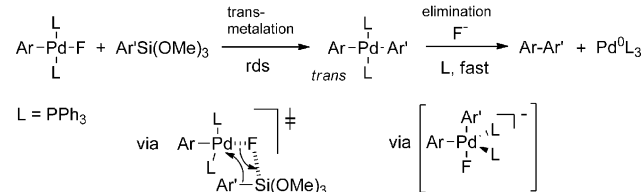


Figure 2. Kinetics of the reaction of $\text{trans-[p-CNC}_6\text{H}_4\text{-Pd-Br(PPh}_3)_2]$ (**6**; $C_0 = 2 \text{ mM}$) with **1** ($\beta = 30$ equiv versus **6**) in the presence of PPh_3 (2 equiv) and $n\text{Bu}_4\text{NF}$ ($\alpha = 25$ equiv versus **6**) in DMF at 70°C . a) Evolution of 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 F^- .

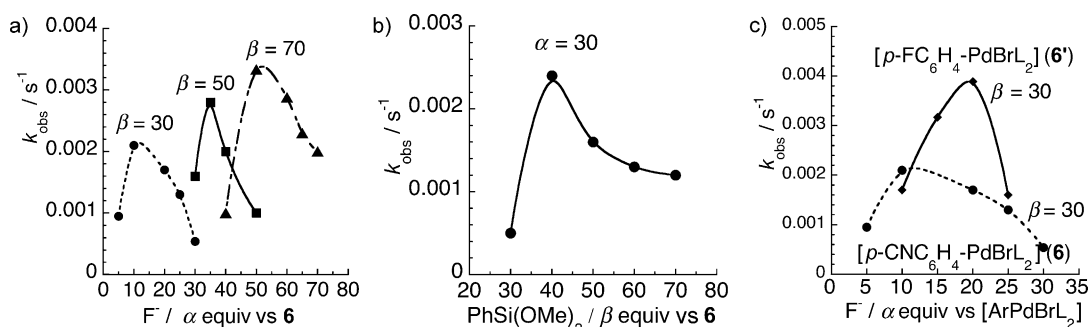


Figure 3. Reaction of **6** (2 mM) with **1** in the presence of F^- (α equiv versus **6**) and PPh_3 (2 equiv) in DMF at 70°C. a) Plot of the pseudo-first-order rate constant k_{obs} versus F^- (α equiv versus **6**) in the presence of **1** ($\beta = 30, 50$ and 70 equiv versus **6**). b) Plot of k_{obs} versus **1** (β equiv versus **6**) in the presence of F^- ($\alpha = 30$ equiv versus **6**). c) Plot of k_{obs} vs F^- (α 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 (α 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.^[8]

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 Ar'Si(OMe)_3 in the rate-determining transmetalation; the second one delivers the unreactive silicate Ar'SiF(OMe)_3^- . As for the Suzuki–Miyaura reaction,^[4a] 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 α values for the same β value (Figure 3c).

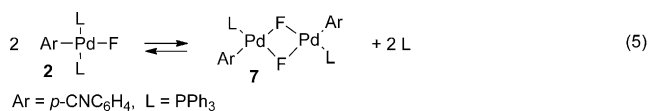
The kinetic laws for the mechanism in Scheme 5 are expressed in Equations (3) and (4).^[9]

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

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

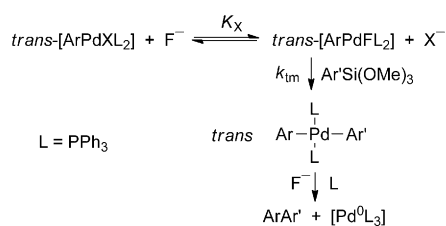
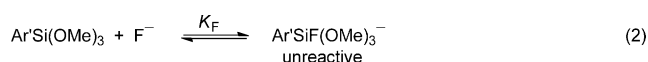
When $[F^-] \ll 1/K_F$ and $[F^-] \ll C_0/(2K_X)$, then $k_{obs} \rightarrow 2k_{tm}\beta K_X[F^-]$, and k_{obs} increases linearly with $[F^-]$ at low concentrations. Conversely, when $[F^-] \gg 1/K_F$ and $[F^-] \gg C_0/(2K_X)$, then $k_{obs} \rightarrow k_{tm}\beta C_0/(K_F[F^-])$ and k_{obs} decreases 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 α/β ratio (0.5, 0.75). Neither **5** nor 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}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).^[4a,5]

The compound **7** was not formed when the isolated **2** was reacted with **1** in the presence of PPh_3 (2 equiv) at room temperature (see Scheme 3). But it was formed from **6** in the presence of F^- , **1**, and PPh_3 (2 equiv) at room temperature.



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

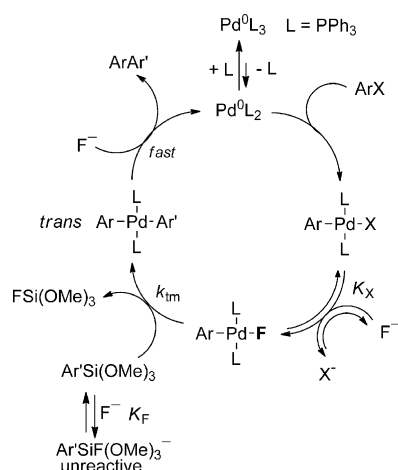
This difference presumably derives from the low thermodynamic concentration of $[\text{ArPdF}(\text{PPh}_3)_2]$, when starting from **6**, which did not allow a fast transmetalation and thus, all the aryl/ Pd^{II} were converted into the unreactive dimer **7** [Eq. (5)]. Upon increasing the temperature, the reaction of **1** with $[\text{ArPdF}(\text{PPh}_3)_2]$, thus leading to 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 PPh_3 (2 equiv) at 25°C, **6** disappeared, but neither 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 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 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 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 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 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 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 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.^[4] 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 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.^[1,2]

Received: January 28, 2014

Revised: March 14, 2014

Published online: May 23, 2014

Keywords: cross-coupling · fluoride · kinetics · palladium · reaction mechanisms

- [1] a) Y. Hatanaka, T. Hiyama, *Tetrahedron Lett.* **1988**, 29, 97–98; b) K.-i. Gouda, E. Hagiwara, Y. Hatanaka, T. Hiyama, *J. Org. Chem.* **1996**, 61, 7232–7233; c) K. Shibata, K. Miyazawa, Y. Goto, *Chem. Commun.* **1997**, 1309–1310; d) E. Mowery, P. DeShong, *Org. Lett.* **1999**, 1, 2137–2140; e) H. M. Lee, S. P. Nolan, *Org. Lett.* **2000**, 2, 2053–2055; f) G. A. Molander, L. Iannazzo, *J. Org. Chem.* **2011**, 76, 9182–9187; g) Y. Hatanaka, T. Hiyama, *Synlett* **1991**, 845–853; h) T. Hiyama, E. Shirakawa, *Organosilicon Compounds in Topics in Current Chemistry*, Vol. 219, Springer, Berlin **2002**, pp. 61–85.
- [2] a) Y. Hatanaka, K.-i. Goda, Y. Okahara, T. Hiyama, *Tetrahedron* **1994**, 50, 8301–8316; b) Y. Hatanaka, T. Hiyama, *J. Am. Chem. Soc.* **1990**, 112, 7793–7794; c) A. Sugiyama, Y.-y. Ohnishi, M. Nakaoka, Y. Nakao, H. Sato, S. Sakaki, Y. Nakao, T. Hiyama, *J. Am. Chem. Soc.* **2008**, 130, 12975–12985.
- [3] a) S. E. Denmark, D. Wehrli, *Org. Lett.* **2000**, 2, 565–568; b) S. E. Denmark, R. F. Sweis, D. Wehrli, *J. Am. Chem. Soc.* **2004**, 126, 4865–4875; c) S. E. Denmark, C. Regens, *Acc. Chem. Res.* **2008**, 41, 1486–1499; d) S. E. Denmark, J. H. C. Liu, *Angew. Chem.* **2010**, 122, 3040–3049; *Angew. Chem. Int. Ed.* **2010**, 49, 2978–2986.
- [4] a) C. Amatore, A. Jutand, G. Le Duc, *Angew. Chem.* **2012**, 124, 2542–2545; *Angew. Chem. Int. Ed.* **2012**, 51, 2492–2503; b) C. Amatore, A. Jutand, G. Le Duc, *Chem. Eur. J.* **2013**, 19, 10082–10093.
- [5] For the synthesis of $[\text{ArPdF}(\text{PPh}_3)_2]$, see: M. C. Pilon, V. V. Grushin, *Organometallics* **1998**, 17, 1774–1781.
- [6] For the characterization of $\text{trans-}[\text{ArPdAr}'(\text{PPh}_3)_2]$, see: C. Adamo, C. Amatore, I. Ciofini, A. Jutand, H. Lakmini, *J. Am. Chem. Soc.* **2006**, 128, 6829–6836.
- [7] For reductive elimination induced by a fifth ligand in square-planar d^{10} complexes, see: a) R. Giovannini, P. Knöchel, *J. Am. Chem. Soc.* **1998**, 120, 11186–11187; b) A. G. Jarvis Amanda, I. J. S. Fairlamb, *Curr. Org. Chem.* **2011**, 15, 3175–3196.
- [8] K. C. Kumara Swamy, V. Chandrasekhar, J. J. Harland, J. M. Holmes, R. O. Day, R. R. Holmes, *J. Am. Chem. Soc.* **1990**, 112, 2341–2348.
- [9] For similar equations in the Suzuki–Miyaura reactions performed in the presence of F^- , see Ref. [4].