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Competition of Insertion and Transmetalation Pathways in the Reactions of Alkenylsilanes with Aryl Complexes of Palladium(II). An Experimental Study[§]

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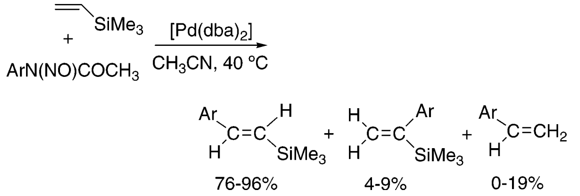
Reactions of alkenylsilanes (alkenyl = 2-propenyl, vinyl, allyl) with neutral and cationic palladium aryl complexes [Pd(C_6F_5)X(NCMe)$_2$] (X = Br, **1**; Cl, **2**), [Pd(C_6F_5)(acac)(NCMe)] (acac = acetylacetonate, **3**), and [Pd(C_6F_5)(bipy)(S)]ClO$_4$ (S = acetone, **4**) were studied. The compounds obtained were substituted alkenylsilanes (formed via Heck substitution) and desilylated olefins (formed by transmetalation followed by reductive elimination or by insertion followed by β-SiMe$_3$ elimination). The analysis of the structure of the final organic products provides a quantitative assessment of the importance of these competing pathways. Transmetalation to palladium was found to be a minor pathway in all cases, whereas insertion of the double bond into the Pd−C_6F_5 bond followed by β-SiMe$_3$ elimination was the major route. The formation of C_6F_5-substituted alkenylsilanes is favored when an excess of starting alkenylsilane is used.

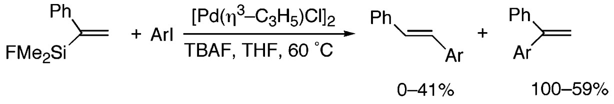
Introduction

The Heck reaction and Hiyama coupling are two useful tools in the realm of C−C coupling reactions catalyzed by palladium complexes. The Heck reaction leads to substituted olefins by reaction of an alkene and an aryl (or vinyl) halide, and the insertion of the alkene into a Pd−aryl (or vinyl) bond is a key step in the catalytic cycle.[1,2] Hiyama coupling is the palladium-catalyzed coupling of organic electrophiles (usually halides or triflates) with organosilane derivatives, and the transmetalation step from silicon to palladium is crucial to the success of the process.[3−6] Both reactions can take place and actually compete in the reactions of alkenylsilanes (either vinyl- or allylsilanes). In fact, a mixture of products with and without a −SiR$_3$ moiety was obtained in the early application of the Pd-catalyzed coupling of alkenylsilanes and aryl electrophiles (eq 1).[7]



(1)

The loss of selectivity reported in this and several other combinations of substrates,[4,5,8−13] in reactions using alkenylsilanes, points to a competition of the routes of insertion and transmetalation. An example of loss of regioselectivity is shown in eq 2, where the percentages of products in the mixture vary depending on the aryl iodide used.[11]



(2)

The formation of both the substituted silanes and the regioisomeric olefins can indeed be explained assuming a competition of the insertion and transmetalation routes, as shown in Scheme 1 for an allylsilane. Transmetalation of the alkenyl group to palladium and reductive elimination leads to the Hiyama coupling product (also called the *ipso* substitution product). A conventional Heck sequence (insertion + β-H

[§] This paper is warmly dedicated to Prof. Antonio Abad (University of Murcia), who prematurely retired due to his health condition.

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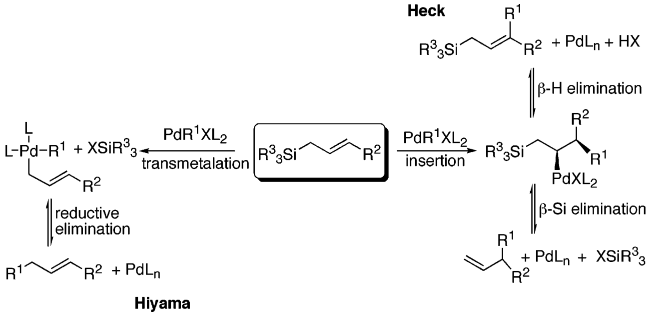
Scheme 1. Competing Reaction Pathways for Unsaturated Silanes and Palladium Organometallic Complexes



elimination) affords substituted alkenylsilanes. However insertion of the alkenylsilane followed by β-Si elimination should produce a regioisomeric C−C coupling compound (a *cine* substitution product). β-Si elimination is less common than the ubiquitous β-H elimination in palladium alkyl complexes, but several clear-cut examples have been reported in the literature.[12,14−16]

The competition of all these reaction pathways will determine the actual ratio of products, and it is interesting to find out when and how much one route is favored over the others.

Several procedures have been developed to enhance the regioselectivity of Pd-catalyzed reactions of alkenylsilanes. Hallberg et al. used silver nitrate to shift the reactions of vinylsilanes or allylsilanes and arylhalides toward the formation of arylated silanes, the product of the Heck reaction.[12,14,17] When this additive is absent, desilylated products, mainly formed by an insertion plus β-Si elimination route, are obtained.[12,14] Phase transfer conditions have also been used to yield the Heck products with higher selectivity.[18] There are also recent reports on the use of functionalized alkenyl(2-pyridyl)dimethylsilanes for the selective preparation of either the Heck products or, if a fluoride source such as tetrabutylammonium fluoride (TBAF) is used as an additive, the Hiyama coupling derivatives.[19] It is known that transmetalation from silicon to palladium can be accelerated using fluorosilicates or silanols (sometimes formed in the reaction medium upon addition of fluoride). Recently, the presence of a hydroxy functionality in aryl- or alkenyl[2-hydroxymethylphenyl]dimethylsilanes has been used to enhance the transmetalation rate of tetraorganosilanes, leading to efficient Hiyama couplings.[20] However slower, transmetalation to palladium has been observed for trimethylsilyl derivatives (the most common silyl derivatives) and cannot be ignored. The formation of palladium allylic complexes from Pd(II) precursors and allylsilanes provides one example.[21]

We have studied the competition of transmetalation and double-bond insertion, choosing as model systems combinations of appropriately substituted alkenyltrimethylsilanes and pentafluorophenyl palladium complexes (the latter have proved to be good models to study both insertion reactions[2] and the transmetalation with stannanes).[22] The prevalence of the reaction routes using different reaction conditions and auxiliary ligands bound to palladium can be deduced by analysis of the final products, and the results are described here.

Results and Discussion

Three alkenyltrimethylsilanes (alkenyl = 2-propenyl, vinyl, and allyl) were reacted with neutral palladium pentafluorophenyl complexes [PdPfX(NCMe)$_2$] (Pf = C_6F_5; X = Br (**1**),[23] Cl (**2**)[24]) and [PdPf(acac)(NCMe)] (acac = acetylacetonate, **3**).[25] Reactions with the cationic derivatives [PdPf(bipy)(S)]ClO$_4$ (S = acetone (**4**), NCMe (**5**)) were also assayed, but complex **5** was eliminated from the tests because of its lower solubility. Complex **4**, prepared in situ in acetone as solvent, was chosen as the model cationic complex for the reactions. Perchlorate was used instead of other common, less hazardous, counterions such as BF_4^- or PF_6^- to avoid any influence of the anion, since we observed that the latter partially reacted with the silyl moiety, giving SiMe$_3$F (detected by ^{19}F NMR). Since the presence of fluoride favors transmetalation, these anions can mask the intrinsic preference of the alkenyltrimethylsilanes for one route over the other and the influence of the Pd(II) precursor in the results obtained. The results for each of the three alkenylsilanes studied are given below.

Reactions with 2-Propenyltrimethylsilane. The reaction of 2-propenyltrimethylsilane with complexes **1**−**4** could follow the reaction pathways depicted in Scheme 2. The product mixtures of the reactions (Table 1) were analyzed in each case by ^{19}F and ^{1}H NMR spectroscopy. All of the compounds observed are framed in Scheme 2. Compounds **6**−**8** and **10** have been reported before;[15,26] nonetheless, the spectra of these compounds and **11** were compared with commercial or independently prepared samples.[27] Compound **9** was separated by preparative TLC and characterized by NMR and MS.

All the reactions start by coordination of the alkenylsilane to palladium through the double bond, leading to **A** (Scheme 2). From that point several reaction routes can follow, and the structure of the final products allows us to trace back the different pathways operating at observable rates in each reaction, according to the following analysis.

(1) Transmetalation from silicon to palladium and reductive elimination (route **a**) leads to 2-pentafluorophenylpropene (**6**), the product of *ipso* substitution.[28]

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(25) Complex **3** exists in CDCl$_3$ solution as a mixture of the monomeric [Pd(acac)Pf(NCMe)] (**3a**, 74%) and a dimeric derivative tentatively assigned to [(acac)PdPf(μ-κ^2-*O,O*-acac)PdPf(NCMe)$_2$] (**3b**, 26%) according to its characteristic ^{1}H and ^{19}F NMR spectra (see Experimental Section).

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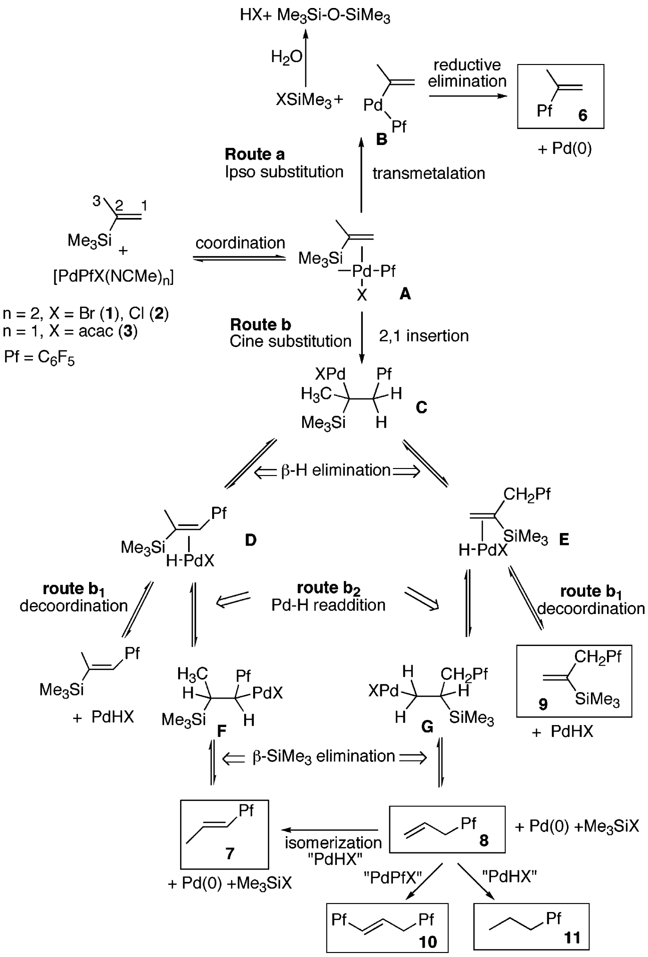
(27) Compound **8** is commercial. Compound **11** can be obtained by hydrogenation of **8** using Wilkinson's catalyst; concomitant isomerization of **8** to the internal olefin **7** is observed. Isomerization of **8** to **7** can also be carried out using the benzylic palladium complex [Pd$_2$(μ-Br)$_2$(η^3-C$_6$F$_5$CH$_2$-CHPh)$_2$] as catalyst (López-Fernández, R.; Albéniz, A. C.; Espinet, P.; Sen, A. *J. Am. Chem. Soc.* **2002**, *124*, 11278−11279). Compound **6** can be obtained, albeit in low yield, by coupling of C$_6$F$_5$MgBr and 2-bromopropene catalyzed by [NiCl$_2$(dppe)] (see Hayashi, T.; Konishi, M.; Okamoto, Y.; Kabeta, K.; Kumada, M. *J. Org. Chem.* **1986**, *51*, 3772−3781 and Woollins, J. D. *Inorganic Experiments*; VCH: Weinheim, 1994).

Scheme 2. Possible Reaction Pathways and Observed Products (framed) of the Reaction of 2-Propenyltrimethylsilane and Palladium Pentafluorophenyl Complexes



(2) 2,1-Insertion of the double bond into the Pd−Pf bond followed by β-H elimination from the methyl group and decoordination leads to the substituted alkenylsilane $CH_2{=}C(SiMe_3)CH_2Pf$ (**9**) in an overall substitution or Heck process (route $\mathbf{b}_1$). Since only the terminal alkenylsilane **9** is observed, β-H elimination of one of the three methyl hydrogens must be always favored versus β-H elimination of a C1 hydrogen (this has also been observed for other closely related alkyls derived from olefin insertion into Pd−C bonds).[29]

(3) Palladium migration to C3 or C1 followed by β-$SiMe_3$ elimination leads to allylpentafluorobenzene (**8**) and 1-pentafluorophenylpropene (**7**), respectively (the products of *cine* substitution, route $\mathbf{b}_2$). The internal alkene **7** can also be formed by isomerization of the terminal alkene **8** in the presence of hydrido-palladium species. According to the preference for β-H elimination from C3 detected in the formation of the silane **9**, **8** should be the main *cine* substitution product and isomerization of this terminal alkene should be the main source of **7**. Two side reactions of **8** are also observed: a Heck substitution to give 1,3-bispentafluorophenylpropene **10** (**8** is less substituted that the starting silane, and its competing coordination should be sterically preferred, whereupon route **b** should lead to **10**) and a hydride transfer to give propylpentafluobenzene (**11**) by reaction with "PdHX" species formed in the course of the reaction; this hydride transfer has been studied in detail before.[30]

Two different mechanisms have been proposed to explain the formation of *cine* substitution products in C−C coupling reactions with alkenyltriorganotin derivatives: (a) insertion of the double bond into a Pd−C bond followed by β-SnR_3 elimination (similar to route $\mathbf{b}_2$), proposed by Kikukawa;[31] and (b) α-SnR_3 elimination to give a palladium carbene complex that decomposes to the final product (proposed by Busacca and Farina).[32] To rule out the intermediacy of a palladium-carbene in the formation of allylpentafluorobenzene (**8**, Scheme 3), we carried out the reaction of 2-propenyltrimethylsilane with complex **1** in the presence of added water. If it were formed, hydrolysis of this electrophilic palladium carbene should lead to a ketone, which was not detected in the reaction mixture. The presence of water did not affect the distribution of products **6**−**11**. Thus, the route depicted in Scheme 2 for the formation of **8** (route $\mathbf{b}_2$) is the most plausible one.

The distribution of products obtained for the different Pd complexes (Table 1) shows that the transmetalation (route **a**) is a minor pathway in all cases. Transmetalation is expected to be less favored for this α-substituted silane when compared to nonsubstituted vinylsilane (see later), but this reluctance does not justify the very low percentages found for $CH_2{=}C(Pf)CH_3$ (**6**). A higher amount of **6** is observed with an increase in the electrophilicity of the Pd center, as clearly shown for the cationic complex **4** (entry 5, Table 1). The chloro-palladium complex **2**, more electrophilic than the Br or acac derivatives **1** and **3**, also shows a slight increase in the amount of **6** formed (entry 3, Table 1) when compared to **1** and **3**. The main route observed is insertion followed by β-$SiMe_3$ elimination (route $\mathbf{b}_2$) to give the *cine* substitution product allylpentafluorobenzene (**8**) (plus its internal isomer **7** and products derived from its further reactions, **10** and **11**; $\sum\mathbf{b}_2$ in Table 1). The Si-containing product $CH_2{=}C(SiMe_3)CH_2Pf$ (**9**) is obtained in low yield in the equimolar reactions of the neutral complexes (entries 1, 3, 4, Table 1) and is absent in the reaction with the cationic complex **4** (entry 5, Table 1). In the latter case the alkenylsilane in intermediate **E** (Scheme 2) is expected to be bound to Pd more strongly in the cationic complex, and substitution promoted by other alkenes present is less favored, so further insertion into the Pd−H bond (route $\mathbf{b}_2$) can occur. When an excess of 2-propenyltrimethylsilane is used (entry 2, Table 1), decoordination of the substituted alkenylsilane by associative substitution promoted by the starting silane occurs (route $\mathbf{b}_1$), and the amount of **9** increases noticeably.

Reactions with Vinyltrimethylsilane. The reactions of complexes **1**−**4** with vinyltrimethylsilane were carried out in the same manner described for 2-propenyltrimethylsilane. Scheme 4 collects, in a simplified way, the plausible reaction routes and products found for this silane (the notation used refers to Scheme 2). Pentafluorostyrene (**12**) is formed by routes **a**

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[28] A less common 1,2 insertion of 2-propenyltrimethylsilane in the Pd−Pf bond followed by β-$SiMe_3$ elimination could also lead to **6**. The occurrence of this route was tested by reacting an equimolar amount of 2-phenylpropene, an alkene electronic and sterically similar to 2-propenyltrimethylsilane, with complex **1**. Only the products of 2,1 insertion, $[Pd(\eta^3\text{-}PhC(Me)CH_2Pf)Br]_2$ and $CH_2Pf\text{-}C(Ph){=}CH_2$, were formed. 2-Phenylpropene was also reacted with complex **4**, and only the products of 2,1 insertion were observed.

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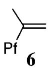
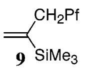
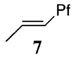
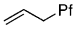
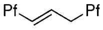
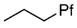
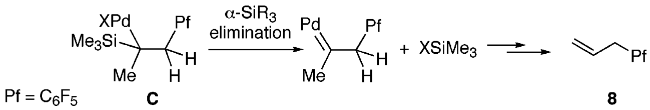
Table 1. Reactions of Complexes 1, 2, 3, and 4 with 2-Propenyltrimethylsilane[a−c]

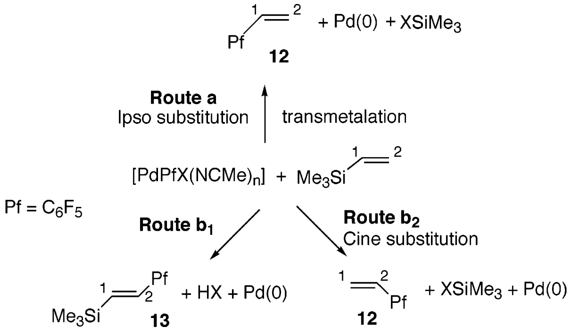
Entry	Pd cpd, (Pd:silane)	Pd cpd	**a**  **6**	**b**$_1$  **9**	Σ**b**$_2$[d]	 **7**	 **8**	 **10**	 **11**	PfH	other
1	**1**, (1:1)	2.3	3.2	3.0	67.5	36.3	7.4	19	4.8	5	19
2	**1**, (1:50)	–	4.2	35.4	50.3	29.3	14.9	3.6	2.5	4	6.1
3	**2**, (1:1)	–	5	2.4	73.9	45.7	6.1	22.1	–	3.2	15.5
4[e]	**3**, (1:1)	1.2	3.5	3.8	81.7	64.6	–	17.1	–	1	4.1
5[f]	**4**, (1:1)	–	15.3	–	71.6	50.6	3.2	17.8	3.2	–	9.9

[a] Pf = C_6F_5. [b] 0.043 mmol of Pd complex and the corresponding amount of silane in $CDCl_3$ (0.6 mL) at room temperature under N_2. [c] The percentages given correspond to the molar amount of products and were determined by integration of ^{19}F NMR signals. The column labeled other shows, in each case, the sum of the percentages of several products that could not be identified. [d] Σ**b**$_2$ = **7** + **8** + **10** + **11**. [e] $[PdPf_2(NCMe)_2]$ is formed (4.7%). [f] Acetone-d_6 as solvent.

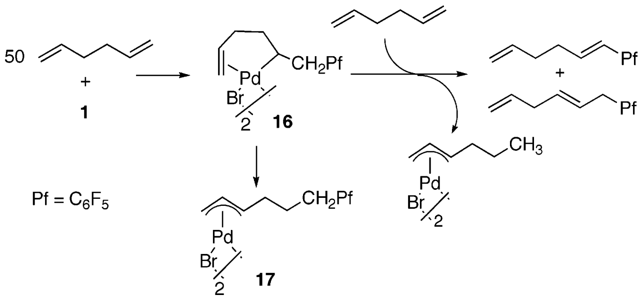
Scheme 3. Alternative Formation of 8 Similar to the Busacca−Farina Route in Organotin C−C Couplings



Scheme 4. Reaction Pathways and Products of the Reaction of Vinyltrimethylsilane and Palladium Pentafluorophenyl Complexes



Scheme 5. Migration Process for Model Complex 16 in the Presence of a High Excess of Alkene



and **b**$_2$, which makes these pathways indistinguishable as far as product structure is concerned. Route **b**$_1$ affords the substituted silane *trans*-PfCH═CHSiMe$_3$ (**13**). Small amounts of the products of side reactions on **12** were also found: Heck reaction, (*E*)-PfCH═CHPf (**14**), and a hydride transfer process, PfCH$_2$-CH$_3$ (**15**).[33]

Table 2 collects the percentages of products obtained in the reactions with different complexes or conditions. Again, desilylated compounds are the major products when a ratio Pd:silane = 1:1 is used (routes **b**$_2$ and **a**), route **b**$_2$ being dominant.[34] In fact, the more electrophilic chloro complex **2** (slightly more prone to transmetalation, see above) shows a lower amount of **12** than complexes **1** and **3**. The same is observed for the cationic complex **4** (entry 5, Table 2).

When the amount of starting silane is increased, a higher amount of *trans*-PfCH═CHSiMe$_3$ (**13**) is obtained. Since vinyltrimethylsilane is less substituted than 2-propenyltrimethylsilane, the associative substitution that takes place in route **b**$_1$ is more favored, and up to 87.8% of **13** can be obtained for a ratio Pd:silane = 1:50 (entry 2, Table 2). Decoordination of **13** aborts route **b**$_2$ (which requires a Pd−H readdition, see Scheme 2), and the amount of PfCH═CH$_2$ (**12**) formed in the conditions of entry 2 (Table 2) could be considered the uppermost limit of transmetalation that occurs for reaction of this silane. However, this could also be the highest amount of **13** that remains coordinated to palladium under these conditions. To test this premise, the isomerization of the enyl palladium complex **16** was monitored in the presence of a 50-fold excess of 1,5-hexadiene (Scheme 5). This process was studied in detail by us before, and we found that in the presence of excess diene associative substitution of the Pf-substituted dienes took place during Pd migration along the hydrocarbon chain leading to free Pf-dienes and nonarylated Pd-allyls.[35] The terminal Pd-allyl **17** is formed if Pd migration occurs all the way, without decoordination of the Pf-diene. Thus, the amount of **17** gives the amount of olefin that does not decoordinate in the process, and for a ratio Pd:1,5-hexadiene = 1:50, the percentage found is 17%. Thus, we can conclude that the amount of **12** in entry 2 (12%, Table 2) may as well be formed by route **b**$_2$.

Reactions with Allyltrimethylsilane. The product distribution of the reaction of allyltrimethylsilane with complexes **1**−**4** cannot be unambiguously correlated with the different routes depicted in Schemes 1 and 2. In the reaction conditions, the formation of intermediate palladium hydrido species leads to the isomerization of the allylsilane to the more stable internal alkene 1-propenyltrimethylsilane. This is a serious drawback since the final products are the result of reaction of both silanes

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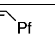
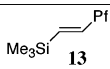
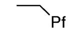
(33) The spectra of compounds **12**−**15** were compared with commercial (**12**) or independently prepared samples. Compound **15** can be obtained by hydrogenation of **12** using Wilkinson's catalyst. Compound **13** can be obtained, in low yield, by coupling of C_6F_5MgBr and 2-bromovinyltrimethylsilane catalyzed by $[NiCl_2(dppe)]$ (see ref 26). Compound **14** can be prepared by reaction of **12** with complex **1** in a Heck-type substitution process (see Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 11504−11505).

(34) The possibility of protonolysis of **13** to give **12** in the reaction conditions was ruled out, since **13** is not affected by HCl(aq) added to a $CDCl_3$ solution of this silane.

(35) Albéniz, A. C.; Espinet P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 4138−4144.

Table 2. Reactions of 1, 2, 3, and 4 with Vinyltrimethylsilane[a−b,c]

Entry	Pd cpd. (Pd:silane)	 **12**	 **13**	 **15**	**other**	**13**:(**12**+**15**)
1	**1**, (1:1)	83.6	10.6	5.8	–	1:8.4
2	**1**, (1:50)	12.2	87.8	–	–	1:0.1
3	**2**, (1:1)	69.7	27.3	3	–	1:2.7
4[d]	**3**, (1:1)	83.1	9.1	–	–	1:9.5
5[e]	**4**, (1:1)	70	–	11.8	18.2	–

[a] Pf = C_6F_5. [b] 0.025 mmol of Pd complex and the corresponding amount of silane in $CDCl_3$ (0.6 mL) at room temperature under N_2. [c] Percentages given correspond to the molar amount of products and were determined by integration of ^{19}F NMR signals. [d] $[PdPf_2(NCMe)_2]$ (4.6%) and **14** (3.2%) are formed. [e] Acetone-d_6 as solvent. The column labeled other shows the sum of the percentages of several products (each one less than 4%) that could not be identified.

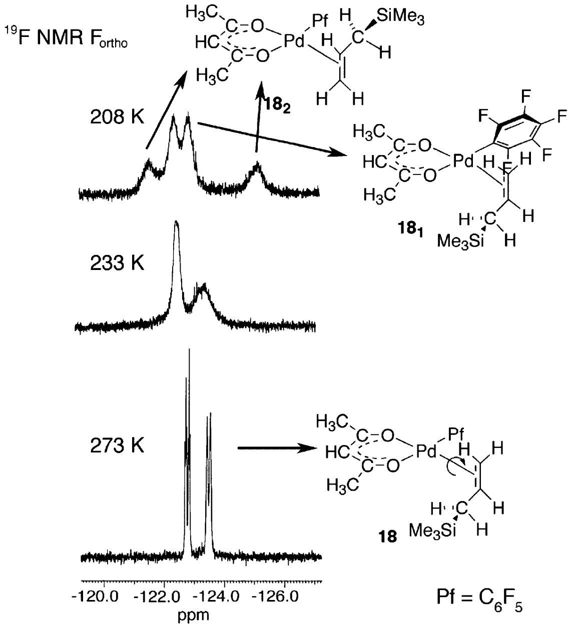


Figure 1. Variable-temperature ^{19}F NMR spectra of complex **18**, showing the effect of hindered rotation of the silane in the F_{ortho} signals of the pentafluorophenyl group.

and some of them arise from two different reaction pathways. Interestingly, an intermediate palladium complex was detected when the reaction of **3** and allyltrimethylsilane was monitored by NMR. It is the silane-bound derivative **18** that could be isolated by carrying out the reaction at low temperature. The complex shows slow rotation of the pentafluorophenyl group about the Pd−C bond at room temperature. However the alkenylsilane undergoes fast rotation about the metal−olefin bond at this temperature; this rotation becomes slow at 208 K with the appearance of two different diastereoisomers ($\mathbf{18}_1$ and $\mathbf{18}_2$, Figure 1), as shown by ^{19}F NMR spectroscopy.[36] Complex **18** corresponds to intermediate **A** in Scheme 2.

No complexes of the type $[PdPf(\eta^3\text{-allyl})L]$ (L = NCMe) or $[Pd(\mu\text{-}Pf)_2(\eta^3\text{-allyl})_2]_2$, coming from transmetalation in the reactions of complexes **1** or **2**, could be detected in the reaction media. This type of allyl(aryl) complexes have been observed by us before, and they are moderately stable in solution, being resistant to reductive elimination unless an electron-withdrawing ligand (such as benzoquinone) is added.[37] The absence of allylic palladium complexes, along with the results obtained for the vinylic silanes (generally more prone to undergo transmetalation), strongly suggests that route **a** does not occur for allyltrimethylsilane.

Conclusions

Transmetalation is a minor route in the reactions of alkenylsilanes and palladium pentafluorophenyl complexes. The reactions with 2-propenyltrimethylsilane allow us to estimate the importance of this pathway in about 4% for the neutral complexes, rising to about 15% for the more electrophilic cationic palladium derivative. Transmetalation using vinyltrimethylsilane is more difficult to quantify, but it represents less than 12% of the amount of final products when the neutral complex **1** is used. There is no evidence of the occurrence of transmetalation in the reactions with allyltrimethylsilane since intermediates of the type $[PdPf(\eta^3\text{-allyl})L]$, known to be stable in the reaction conditions, have not been detected. Insertion of the double bond into the Pd−Pf bond followed by β-$SiMe_3$ elimination to give desilylated *cine* substitution products is the major route in all cases. These results estimate the inherent preference of trimethylalkenylsilanes for one route over the other. It should be kept in mind that in the presence of other additives such as fluorides, as it is sometimes the case in catalytic experiments, the relative importance of both routes can be different.

The Heck arylation of alkenylsilanes can be favored by using an excess of reactant silane to promote the associative substitution of the arylated silane.

Experimental Section

General Considerations. ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded on Bruker AC-300 and ARX-300 instruments. Chemical shifts are reported in δ (ppm) and referenced to Me_4Si (^1H and ^{13}C) or $CFCl_3$ (^{19}F). All of the NMR spectra were recorded at 293 K unless otherwise noted. Organic products were analyzed using a HP-5890 gas chromatograph connected to a HP-5988 mass spectrometer at an ionizing voltage of 70 eV using a quadrupole analyzer. Elemental CHN analyses were determined with a Perkin-Elmer 2400 CHN microanalyzer. IR spectra were recorded with a Perkin-Elmer FT 1720 X spectrophotometer. All the reactions described were carried out in a nitrogen atmosphere.

Solvents were dried over CaH_2, distilled, and deoxygenated prior to use. 2-Propenyltrimethylsilane, vinyltrimethylsilane, 1,5-hexadiene, and 2-phenylpropene were purchased from Aldrich and Lancaster. The palladium complexes $[PdPfX(NCMe)_2]$ (X = Br, **1**;[23] X = Cl, **2**[24]) and [PdBrPf(bipy)][38] were prepared according to

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[36] The slow limit exchange in the ^1H NMR spectrum is not reached at this temperature, and only extremely broad signals for the coordinated allylsilane are observed.

[37] Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B. *Chem. Eur. J.* **2001**, *7*, 2481−2489.

[38] Usón, R.; Fornies, J.; Nalda, J. A.; Lozano, M. J.; Espinet, P.; Albéniz, A. C. *Inorg. Chim. Acta* **1989**, *156*, 251−256.

literature procedures. Compounds **6**,[15] **7**,[15] **8**,[15,26] **10**,[15] **12**,[15] **14**,[15] **16**,[35] and **17**[35] have been described before.

Caution: Perchlorate salts are potentially explosive and should be prepared and handled in only small amounts, exercising all necessary care for this kind of hazardous explosive materials. For purposes different from the use in this mechanistic study perchlorate can be substituted by tetrafluoroborate, hexafluorophosphate, triflate, or similar weakly coordinating anions.

Synthesis of NBu$_4$[PdBrPf(acac)]. To a solution of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_2Pf_2]$[38] (1.3930 g, 1.031 mmol) in CH_2Cl_2 (30 mL) was added Tl(acac) (0.6256 g, 2.061 mmol). The mixture was stirred in the absence of light for 1.5 h at room temperature. After that time, the suspension was filtered and the resulting solution was evaporated to dryness. Et_2O (20 mL) was added to the residue, and upon cooling orange crystals were obtained. The crystals were filtered, washed with Et_2O, and air-dried. Isolated yield: 1.3351 g (93%). Anal. Calcd for $C_{27}H_{43}BrF_5NO_2Pd$: C, 46.66; H, 6.24; N, 2.02. Found: C, 46.90; H, 5.97; N, 2.31. ^{19}F NMR (282 MHz, $CDCl_3$): δ −165.8 (m, 2F$_{meta}$), −163.7 (t, 1F$_{para}$), −118.8 (m, 2F_{ortho}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.25 (s, 1H; CH$_{acac}$), 3.37 (m, 8H; CH_2^{α}), 1.92 (s, 3H; Me$_{acac}$), 1.81 (s, 3H; Me$'_{acac}$), 1.68 (m, 8H; CH_2^{β}) 1.45 (m, 8H; CH_2^{γ}), 0.96 (t, J = 8.9 Hz, 12H; CH_3). IR (cm^{-1}): ν 1630 (s), 1497 (m), 1054 (s), 954 (s), 782 (s), Pf; 884 (m), NBu$_4^+$; 257 (m), Pd−Br; 1596 (s), 1581 (s), C═O.

Synthesis of [PdPf(acac)(NCMe)] (3). To a solution of $AgBF_4$ (0.1710 g, 0.878 mmol) in NCMe (30 mL) was added NBu$_4$[PdBrPf(acac)] (0.6104 g, 0.878 mmol). The mixture was stirred in the absence of light for 1 h at room temperature. After that time, the suspension was filtered and the resulting solution was evaporated to dryness. The residue was extracted with Et_2O (6 × 10 mL), and NCMe (0.5 mL) was added to the ethereal solution. This solution was concentrated to 3 mL, and *n*-hexane (0.5 mL) was added. The solution was cooled to −20 °C to yield yellow crystals, which were filtered, washed with cold Et_2O, and air-dried. Several additional fractions of pure yellow crystals were collected from the mother liquors by cooling. Isolated total yield: 0.2213 g (61%). Anal. Calcd for $C_{13}H_{10}F_5NO_2Pd$: C, 37.75; H, 2.44; N, 3.39. Found: C, 37.78; H, 2.40; N, 3.49. IR (cm^{-1}): ν 1630 (s), 1497 (m), 1054 (s), 954 (s), 782 (s), Pf; 1595 (s), 1579 (s), C═O; 2355 (m), 2310 (m), NCMe.

Complex **3** exists in $CDCl_3$ solution as a mixture of the complexes [PdPf(acac)(NCMe)] (**3a**, 74%) and a dimeric derivative tentatively assigned to [(acac)PdPf(μ-κ^2-*O*,*O*-acac)PdPf(NCMe)$_2$] (**3b**, 26%).

3a: ^{19}F NMR (282 MHz, $CDCl_3$): δ −164.1 (m, 2F$_{meta}$), −160.5 (t, 1F$_{para}$), −123.3 (m, 2F_{ortho}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.40 (s, 1H; CH$_{acac}$), 2.30 (s, 3H; NCMe), 2.05 (s, 3H; Me$_{acac}$), 1.9 (s, 3H; Me$'_{acac}$).

3b: ^{19}F NMR (282 MHz, $CDCl_3$): δ −164.9 (m, 1F$_{meta}$), −163.5 (m, 2F$_{meta}$), −163.2 (m, 1F$_{meta}$), −160.5 (t, 1F$_{para}$), −159.1 (t, 1F$_{para}$), −124.8 (m, 2F_{ortho}), −122.5 (m, 1F_{ortho}), −121.5 (m, 1F_{ortho}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.38 (s, 1H; CH$_{acac}$), 5.05 (s, 1H; CH$_{acac'}$), 2.52 (s, 3H; Me$_{acac'}$), 2.38 (s, 6H; NCMe), 2.35 (s, 3H; Me$_{acac'}$), 2.12 (s, 3H; Me$_{acac}$), 1.90 (s, 3H; Me$_{acac}$).

Synthesis of [PdPf(bipy)(NCMe)]ClO$_4$ (5). To a solution of $AgClO_4$ (0.0317 g, 0.153 mmol) in NCMe (30 mL) was added [PdBrPf(bipy)] (0.0779 g, 0.153 mmol). The mixture was stirred in the absence of light for 6 h at room temperature. After that time, the suspension was filtered and the resulting solution was evaporated to dryness. The residue was treated with Et_2O (20 mL) and stirred to yield a white solid, which was filtered, washed with Et_2O, and air-dried. Isolated yield: 0.0721 g (82%). Anal. Calcd for $C_{18}H_{11}ClF_5N_3O_4Pd$: C, 37.92; H, 1.94; N, 7.37. Found: C, 37.57; H, 2.09; N, 6.98. ^{19}F NMR (282 MHz, CD_3CN): δ −162.9 (m, 2F$_{meta}$), −159.7 (t, 1F$_{para}$), −121.2 (m, 2F_{ortho}). ^{1}H NMR (300 MHz, CD_3CN): δ 8.65 (d, J = 6.4 Hz, 1H; H$^{6'}_{bipy}$), 8.35 (m, 3H; H$^{3,3',4'}_{bipy}$), 8.22 (t, J = 6.4 Hz, 1H; H$^4_{bipy}$), 7.88 (d, J = 6.4 Hz, 1H; H$^6_{bipy}$), 7.80 (t, J = 6.4 Hz, 1H; H$^{5'}_{bipy}$), 7.45 (t, J = 6.4 Hz, 1H; H$^5_{bipy}$), 2.18, (s, 3H; NCMe). IR (cm^{-1}): ν 1630 (w), 1497 (m), 1054 (s), 954 (s), 782 (s), Pf; 2330 (m), 2310 (m), NCMe; 1614 (m), bipy; 1090 (br), ClO$_4^-$.

Synthesis of Solutions of [PdPf(bipy){(CD$_3$)$_2$CO}]ClO$_4$ (4). To a solution of $AgClO_4$ (0.0071 g, 0.034 mmol) in acetone-d_6 (1 mL) was added [PdBrPf(bipy)] (0.0174 g, 0.034 mmol). The mixture was filtered to yield a yellow solution of complex **4** in acetone-d_6. A stoichiometric amount of 2-propenyltrimethylsilane and vinyltrimethylsilane were added to the samples of **4** prepared according to this procedure. ^{19}F NMR (282 MHz, $(CD_3)_2CO$): δ −162.2 (m, 2F$_{meta}$), −159.0 (t, 1F$_{para}$), −120.2 (m, 2F_{ortho}). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 8.70 (d, J = 6.4 Hz, 1H; H$^{6'}_{bipy}$), 8.45 (m, 4H; H$^{3,4,3',4'}_{bipy}$), 8.15 (d, J = 6.4 Hz, 1H; H$^6_{bipy}$), 7.92 (t, J = 6.4 Hz, 1H; H$^{5'}_{bipy}$), 7.68 (t, J = 6.4 Hz, 1H; H$^5_{bipy}$).

Reactions of Neutral Palladium Complexes with 2-Propenyltrimethylsilane. 2-Propenyltrimethylsilane (0.007 mL, 0.043 mmol) was added under N_2 to a solution of **1** (0.0186 g, 0.043 mmol) in $CDCl_3$ (0.6 mL) in an NMR tube. The reaction was monitored by ^{19}F and ^{1}H NMR, and the formation of **6**,[15] **7**,[15,26] **8**,[15,26] **9**, **10**,[15] **11**, and PfH was observed as described in the text.

9: ^{19}F NMR (282 MHz, $CDCl_3$): δ −163.5 (m, 2F$_{meta}$), −157.9 (t, 1F$_{para}$), −143.9 (m, 2F_{ortho}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.38 (s, 1H; H^1),* 5.21 (s, 1H; H$^{1\prime}$),* 3.49 (s, 2H; H^2), 0.12 (s, 9H; SiMe$_3$). MS (EI, 70 eV): *m*/*z* (relative intensity) 280 (M$^+$, 2), 265 (100), 181 (35), 169 (13), 77 (40), 73 (37), 43 (24). *H^1 = H *cis* to CH$_2$−Pf, H$^{1\prime}$ = H *trans* to CH$_2$−Pf.

11: ^{19}F NMR (282 MHz, $CDCl_3$): δ −163.7 (m, 2F$_{meta}$), −158.8 (t, 1F$_{para}$), −144.9 (m, 2F_{ortho}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.69 (t, J_{12} = 8.0 Hz, 2H; H^1), 1.62 (m, 2H; H^2), 0.95 (t, J_{32} = 8.0 Hz, 3H; H^3).

The same procedure was used for the reactions collected in Table 1 with the neutral palladium complexes **2** and **3** or using solutions of **4** (prepared as described above). In some experiments small amounts of complex [PdPf$_2$(NCMe)$_2$] are observed: ^{19}F NMR (282 MHz, $CDCl_3$): δ −164.5 (m, 2F$_{meta}$), −161.0 (t, 1F$_{para}$), −117.5 (m, 2F_{ortho}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 6H; NCMe).

The reaction of Table 1, entry 2 was carried out in a preparative scale. Complex **1** (0.0675 g, 0.155 mmol) and 2-propenyltrimethylsilane (1.23 mL, 7.75 mmol) were mixed in CH_2Cl_2 for 5 min. The solvent was evaporated, and the product mixture was separated by preparative TLC using an *n*-hexane/ethyl acetate (3:1) mixture as eluent. Compound **9** was separated in the lowest R_f band.

Reaction of 1 with 2-Phenylpropene. 2-Phenylpropene (0.003 mL, 0.024 mmol) was added under N_2 to a solution of **1** (0.0104 g, 0.024 mmol) in $CDCl_3$ (0.6 mL) in an NMR tube. The reaction was monitored by ^{19}F and ^{1}H NMR, and the formation of the benzylic complex [Pd(η^3-PhC(Me)CH$_2$Pf)Br]$_2$ and PfCH$_2$C(Ph)═CH$_2$ was observed as described in ref 24.

[Pd(η^3-PhC(Me)CH$_2$Pf)Br]$_2$: ^{19}F NMR (282 MHz, $CDCl_3$): δ −162.5 (m, 2F$_{meta}$), −156.2 (t, 1F$_{para}$), −140.8, (m, 2F_{ortho}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (m, 2H; H$^{3,5}_{Ph}$), 7.45 (t, 1H; H$^2_{Ph}$), 7.30 (m, 1H; H$^4_{Ph}$), 6.6 (br, 1H; H$^6_{Ph}$), 3.10 (d, J = 16.0 Hz, 1H; C*H*H−Pf), 2.75 (d, J = 16.0 Hz, 1H; CH*H*−Pf), 1.32 (s, 3H; Me).

PfCH$_2$C(Ph)═CH$_2$: ^{19}F NMR (282 MHz, $CDCl_3$): δ −163.0 (m, 2F$_{meta}$), −156.0 (t, 1F$_{para}$), −143.2, (m, 2F_{ortho}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.38 (s, 1H; H^1),* 4.85 (s, 1H; H$^{1\prime}$),* 3.75 (s, 2H; H^2). *H^1 = H *cis* to Ph, H$^{1\prime}$ = H *trans* to Ph.

Reactions of Neutral Palladium Complexes with Vinyltrimethylsilane. Vinyltrimethylsilane (0.1203 mL of a 0.208 M solution in $CDCl_3$ titrated by ^{1}H NMR with naphthalene as standard, 0.025 mmol) was added under N_2 to a solution of **1** (0.0109 g, 0.025 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube. The reaction was monitored by ^{19}F and ^{1}H NMR and the formation of **12**,[15] **13**, **14**,[15] and **15** was observed as described in the text.

13: ^{19}F NMR (282 MHz, $CDCl_3$): δ −163.7 (m, 2F$_{meta}$), −156.8 (t, 1F$_{para}$), −145.0 (m, 2F_{ortho}). ^{1}H NMR (300 MHz, $CDCl_3$): δ

6.83, 6.72 (AB system, $J = 18.7$ Hz, 2H; CH═CH), 0.17 (s, 9H; SiMe$_3$). MS (EI, 70 eV): m/z (relative intensity) 266 (M$^+$, 5), 251 (100), 169 (40), 77 (56).

15: ^{19}F NMR (282 MHz, CDCl$_3$): δ −163.5 (m, 2F$_{\mathrm{meta}}$), −159.0 (t, 1F$_{\mathrm{para}}$), −145.8 (m, 2F_{orto}). ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.75 (q, $J = 8.0$ Hz, 2H; H^1), 1.20 (t, $J = 8.0$ Hz, 3H; H^2).

The same procedure was used for the experiments collected in Table 2 starting from the corresponding complex or solution of **4** in acetone-d_6 as described above.

In the reaction of **1** with vinyltrimethylsilane in CD$_3$CN the complex [PdPf$_2$(NCMe)$_2$] is observed.

Reaction of 1 with 1,5-Hexadiene.[35] 1,5-Hexadiene (0.147 mL, 1.238 mmol) was added under N$_2$ to a solution of **1** (0.0108 g, 0.025 mmol) in CDCl$_3$ (0.5 mL) in an NMR tube. The reaction was monitored by ^{19}F and ^{1}H NMR, and final products were 1-Pf-1,5-hexadiene (4%), 1-Me-5-Pf-cyclopentene (8%), 6-Pf-1,4-hexadiene (71%), and **17** (17%).

Synthesis of [PdPf(acac)(Me$_3$SiCH$_2$CH═CH$_2$)] (18). To a solution of **3** (0.0775 g, 0.187 mmol) in CH$_2$Cl$_2$ (5 mL) at 273 K was added allyltrimethylsilane (0.1070 g, 0.937 mmol). The mixture was stirred at 273 K for 2 h, and the resulting solution was treated with activated carbon and filtered through magnesium sulfate. The filtrate was evaporated to ca. 0.5 mL, and a yellow solid precipitated upon addition of n-hexane (5 mL). The supernatant solution was decanted off, and the solid was dried in vacuo. Isolated yield: 0.040 g (44%). Anal. Calcd for C$_{17}$H$_{21}$F$_5$O$_2$PdSi: C, 41.94; H, 4.35. Found: C, 41.64; H, 3.95. ^{19}F NMR (282 MHz, CDCl$_3$): δ −162.9 (m, 2F$_{\mathrm{meta}}$), −159.72 (t, 1F$_{\mathrm{para}}$), −122.9 (m, 1F_{ortho}), 123.5 (m, 1F_{ortho}). ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.85 (m, 1H; H^2), 5.45 (s, 1H; CH$_{\mathrm{acac}}$), 4.57 (d, $J = 9.0$ Hz, 1H; H^1), 4.38 (d, $J = 13.8$ Hz, 1H; H$^{1'}$), 2.09 (dd, $J = 11.7$, 4.7 Hz, 1H; H^3), 1.98 (s, 3H; Me$'_{\mathrm{acac}}$), 1.92 (s, 3H; Me$_{\mathrm{acac}}$), 1.57 (t, $J = 11.7$ Hz, 1H; H$^{3'}$), 0.05 (s, 9H; SiMe$_3$). IR (cm^{-1}): ν 1630 (w), 1497 (s), 1054 (s), 954 (s), 782 (s), Pf; 1584 (s), CO; 1271 (w), 852 (s), Si−Me$_3$.

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Supporting Information Available: Figures containing ^{19}F and ^{1}H NMR spectra of reaction mixtures and compound **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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