Reaction of Diazonium Salts with Transition Metals. Part 11.[1] Palladium-catalyzed Aryldesilylation of Alkenylsilanes by Arenediazonium Salts

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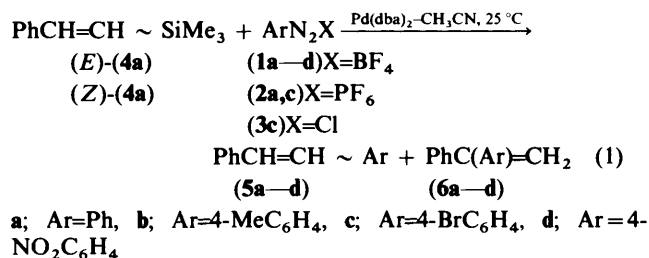
Under palladium(0) catalysis, both (E)- and (Z)-$RCH=CHSiMe_3$($R=Rh$, 4-MeC_6H_4, 4-$NO_2C_6H_4$, n-C_6H_{13}, and $MeOCH_2$) were easily aryldesilylated by ArN_2X ($Ar=Ph$, 4-MeC_6H_4, 4-BrC_6H_4 and 4-$NO_2C_6H_4$; $X=BF_4$, PF_6, and Cl) to give (E)-$RCH=CHAr$ and $RC(Ar)=CH_2$ as the main products at 25 °C in acetonitrile. *anti*- and *syn*-1,2-Elimination of $Pd(0)$ and Me_3Si from the adducts, *threo*- and *erythro*-$RCH(PdX)CHSiMe_3$, generated from $ArPdX$ and (E) and (Z)-$RCH=CHSiMe_3$, respectively, are proposed for the formation of (E)-$RCH=CHAr$ from either isomer of $RCH=CHSiMe_3$.

Over the past ten years, alkenylsilanes have been increasingly used in organic synthesis as key intermediates. The reactivity of alkenylsilanes with a variety of electrophiles by regio- and stereo-specific pathways is now well documented.[2] However, few transition metal-mediated reactions *via* alkenylsilanes have been reported because of the low reactivity of the Si–C bond towards transmetallation. Reactions of (E)-$PhCH=CHSiMe_3$ or (E)-$PhCH=CHSiF_5^-$ with palladium salts[2] have been described to form (E)-$PhCH=CH-Pd-$intermediates with retention of their geometry through an addition–elimination[3] or a transmetallation[4] mechanism. Unfortunately, the corresponding (Z)-isomers were not investigated in these reactions.

Palladium-catalyzed reactions of arenediazonium salts (ArN_2X) involve an arylpalladium species $(ArPdX)$ as a key intermediate.[1,5-8] In a preliminary communication,[9] we reported that both (E)- and (Z)-$PhCH=CHSiMe_3$ were easily aryldesilylated by $[ArPd]^+BF_4^-$ generated from ArN_2BF_4 and bis(dibenzylideneacetone)palladium(0) $[Pd(dba)_2]$ to give (E)-$PhCH=CHAr$ and $PhC(Ar)=CH_2$, but not (Z)-$PhCH=CHAr$. The palladium-catalyzed reaction of $CH_2=CHSiMe_3$ with ArN_2BF_4 gave $ArCH=CH_2$, (E)-$ArCH=CHSiMe_3$ and $ArC(SiMe_3)=CH_2$.[10] We now wish to report the palladium-catalyzed reactions of (E)- and (Z)-$RCH=CHSiMe_3$($R=aryl$ and alkyl) with $ArN_2X(X=BF_4$, PF_6, and Cl), and their stereochemical features.

Results and Discussion

No appreciable reactions of the alkenylsilanes with ArN_2X could be observed in the absence of a palladium catalyst. The addition of $Pd(dba)_2$ (5 mol%) to a solution of (E)-$PhCH=CHSiMe_3$ $[(E)$-$(4a)]$ and ArN_2BF_4 $(1a$—$d)$ in aceto-nitrile at 25 °C caused a rapid gas evolution and gave a clear yellow solution. A g.c. analysis of the reaction mixture and n.m.r. analysis of the isolated products showed the formation of (E)-$PhCH=CHAr[(E)$-$(5a$—$d)]$ and $PhC(Ar)=CH_2(6a$—$d)$ [Equation (1)]. The results are summarized in Tables 1 and 2.

$$PhCH=CH \sim SiMe_3 + ArN_2X \xrightarrow{Pd(dba)_2-CH_3CN, \ 25 \ °C}$$

(E)-$(4a)$ $(1a$—$d)X=BF_4$

(Z)-$(4a)$ $(2a,c)X=PF_6$

$(3c)X=Cl$

$$PhCH=CH \sim Ar + PhC(Ar)=CH_2 \quad (1)$$

$(5a$—$d)$ $(6a$—$d)$

a; $Ar=Ph$, b; $Ar=4$-MeC_6H_4, c; $Ar=4$-BrC_6H_4, d; $Ar=4$-$NO_2C_6H_4$

More than a trace of (Z)-(5) could not be detected in all the reactions with $(1a$—$d)$. Both electron-donating and -withdrawing groups on (1) could be used successfully and the arylated styrenes were obtained in quantitative yields in the reactions with (E)-$(4a)$, although the electron-withdrawing groups reduced the rates considerably and increased the isomer ratio, $(5):(6)$.

Entries 4 and 5 in Table 1 show the effects of substituents on the aromatic ring of compound (E)-(4) in the reaction with $(1a)$ [Equation (2)]. The rate in this case was more sensitive to the presence of both electron-donating and -withdrawing groups on compound (4) as compared to those on compound (1).

The reactions with (Z)-$(4a)$ required more than 10 mol% of $Pd(dba)_2$ to obtain reasonable yields and rates. Unexpectedly compound (Z)-(5) was not observed in the arylated products. Neither of starting alkenylsilanes (E)- and (Z)-$(4a)$, isomerized during the reactions, although very slow isomerization of (Z)-$(4a)$ to (E)-$(4a)$ was observed when the reaction mixture was allowed to stand for a few days at room temperature. A control reaction of compound $(1b)$ with (E)- or (Z)-$(4a)$ in the presence of (E)- and (Z)-$(5a)$ clearly showed that no isomerization occurred in either product isomer, (E)- and (Z)-$(5a)$, under these particular reaction conditions. In the reaction with (Z)-$(4a)$, the electron-withdrawing groups on compound (1) did not decrease the rates but rather accelerated them.

The effects of the counter anion of ArN_2X are summarized in Table 3. ArN_2PF_6 (2) also could be favourably used in the
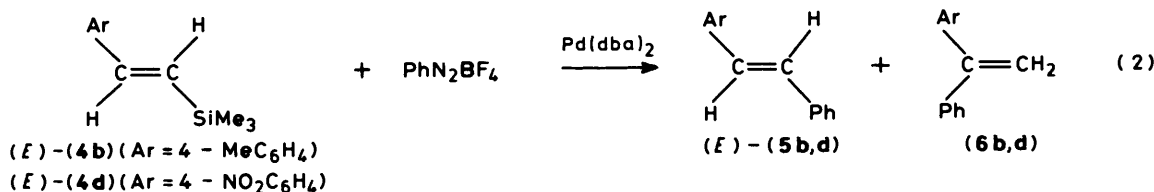

(E)-$(4b)(Ar = 4 - MeC_6H_4)$

(E)-$(4d)(Ar = 4 - NO_2C_6H_4)$

(E)-$(5b,d)$

$(6b,d)$

Table 1. Palladium-catalyzed aryldesilylation of (E)-ArCH=CHSiMe$_3$[(E)-(4a—d)] by ArN$_2$BF$_4$ (1a—d) [Equations (1) and (2)]

Entry	Ar in ArHC=CHSiMe$_3$	Ar in ArN$_2$BF$_4$	Pd(dba)$_2$ (mol %)	Rates[a] (% min^{-1})	Yields[b] (%)	Products (% ratio)[c] PhHC=CHAr	Ph(Ar)C=CH$_2$
1	Ph[(E)-(4a)]	Ph(1a)	2	4.1	81	(E)-(5a) (76)	(6a) (24)
2	(E)-(4a)	(1a)	5	13	98	(E)-(5a) (67)	(6a) (33)
3	(E)-(4a)	(1a)	20	47	99	(E)-(5a) (57)	(6a) (43)
4	4-Me-C$_6$H$_4$-[(E)-(4b)]	(1a)	5	22	100	(E)-(5b) (74)	(6b) (26)
5	4-NO$_2$-C$_6$H$_4$-[(E)-4d)]	(1a)	5	0.31	67	(E)-(5d) (65)	(6d) (35)
6	(E)-(4a)	4-Me-C$_6$H$_4$-(1b)	5	16	97	(E)-(5b) (58)	(6b) (42)
7	(E)-(4a)	4-Br-C$_6$H$_4$-(1c)	5	9.4	100	(E)-(5c) (65)	(6c) (35)
8	(E)-(4a)	4-NO$_2$-C$_6$H$_4$-(1d)	5	4.6	99	(E)-(5d) (86)	(6d) (14)

[a] Steady state rates at early stage estimated by the gas evolution. [b] g.c. yields based on the amount of compound (1) used. [c] Determined by g.c.

Table 2. Palladium-catalyzed aryldesilylation of (Z)-PhCH=CHSiMe$_3$[(Z)-(4a)] by ArN$_2$BF$_4$ (1a—d) [Equation (1)]

Entry	Ar in ArN$_2$BF$_4$	Pd(dba)$_2$ (mol %)	Rate[a] (% min^{-1})	Yield[b] (%)	Products (% ratio)[c] PhHC=CHAr	Ph(Ar)C=CH$_2$
9	Ph-(1a)	5	3.0	14	(E)-(5a) (76)	(6a) (24)
10	(1a)	10	7.7	97	(E)-(5a) (80)	(6a) (20)
11	(1a)	20	30	100	(E)-(5a) (74)	(6a) (26)
12	4-MeC$_6$H$_4$-(1b)	5	3.1	54	(E)-(5b) (74)	(6b) (26)
13	(1b)	10	5.2	68	(E)-(5b) (70)	(6b) (30)
14	4-BrC$_6$H$_4$-(1c)	5	4.3	45	(E)-(5c) (64)	(6c) (36)
15	(1c)	10	6.0	100	(E)-(5c) (76)	(6c) (24)
16	4-NO$_2$C$_6$H$_4$(1d)	5	6.4	77	(E)-(5d) (75)	(6d) (25)
17	(1d)	10	8.2	84	(E)-(5d) (76)	(6d) (24)

[a] Steady state rates at early stage estimated by the gas evolution. [b] g.c. yields based on the amount of compound on (1) used. [c] Determined by g.c.

Table 3. Effects of counter anion of ArN$_2$X(1—3) on palladium-catalyzed aryldesilylation of (E)- and (Z)-PhCH=CHSiMe$_3$(4a) by ArN$_2$X [Equation (1)]

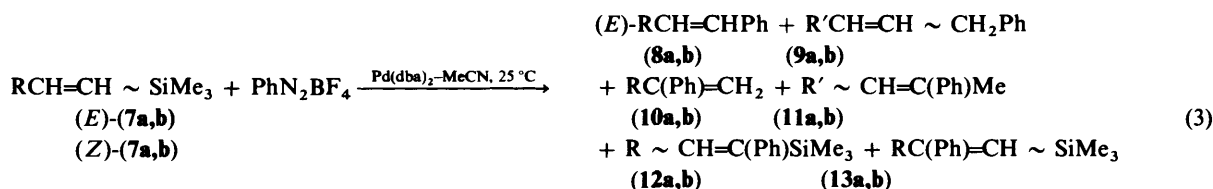| Entry	(E) or (Z) (4a)	ArN$_2$X Ar; X	Pd(dba)$_2$ (mol %)	Rates[a] (% min^{-1})	Yields[b] (%)	Products (% ratio)[c] HPhC=CHAr	HPhC=CHAr	Ph(Ar)C=CH$_2$
1	(E)	Ph; BF$_4$ (1a)	5	13	98	(E)-(5a) (67)		(6a) (33)
18	(E)	Ph; PF$_6$ (2a)	5	28	86	(E)-(5a) (85)		(6a) (15)
7	(E)	4-BrC$_6$H$_4$; BF$_4$ (1c)	5	9.4	100	(E)-(5c) (65)		(6c) (35)
19	(E)	4-BrC$_6$H$_4$PF$_6$ (2c)	5	10	100	(E)-(5c) (86)		(6c) (14)
20	(E)	4-BrC$_6$H$_4$; Cl (3c)	5	4.3	14	(E)-(5c) (94)	(Z)-(5c) (6)	(6c) (trace)
21	(E)	(3c)	20		37	(E)-(5c) (95)	(Z)-(5c) (5)	(6c) (trace)
14	(Z)	(1c)	5	4.3	45	(E)-(5c) (64)		(6c) (36)
22	(Z)	(2c)	5		100	(E)-(5c) (86)		(6c) (14)
23	(Z)	(3c)	18		22	(E)-(5c) (90)	(Z)-(5c) (7)	(6c) (3)

[a] Steady state rates at early stage estimated by the gas evolution. [b] g.c. yields based on ArN$_2$X used. [c] Determined by g.c.

Table 4. Palladium-catalyzed reactions of n-C$_6$H$_{13}$CH=CHSiMe$_3$(7a) and MeOCH$_2$CH=CHSIMe$_3$ (7b) with PhN$_2$BF$_4$ (1a) [Equation (3)]

Entry	Silane	Pd(dba)$_2$ (mol %)	Yield[a] (%)	Products, % ratio[b] (8)	(9)	(10)	(11)	(12) (E/Z)	(13) (E/Z)	Unknown
24	(E)-(7a)	3	76	18	11	39	21	6(0/100)	2(100/0)	3
25	(Z)-(7a)	5	71	17	17	36	17	9(78/22)	5(60/40)	10
26	(E)-(7b)	5	(23)[c]	0	0	66	16	5		13[d]
27	(Z)-(7b)	20	(13)[c]	0	0	56	41	Trace		3[d]

[a] Unless otherwise noted g.c. yields based on (1a). [b] Determined by g.c. [c] Isolated yields based on the amount of compound (1a) used. [d] PhCH=CHCHO was present.

$$(E)\text{-RCH=CHPh} + R'CH=CH \sim CH_2Ph$$
$$\text{(8a,b)} \qquad\qquad \text{(9a,b)}$$

$$RCH=CH \sim SiMe_3 + PhN_2BF_4 \xrightarrow{\text{Pd(dba)}_2\text{—MeCN, 25 °C}} + RC(Ph)=CH_2 + R' \sim CH=C(Ph)Me$$
$$(E)\text{-(7a,b)} \qquad\qquad\qquad \text{(10a,b)} \qquad\qquad \text{(11a,b)} \qquad\qquad (3)$$
$$(Z)\text{-(7a,b)} \qquad\qquad\qquad + R \sim CH=C(Ph)SiMe_3 + RC(Ph)=CH \sim SiMe_3$$
$$\text{(12a,b)} \qquad\qquad\qquad \text{(13a,b)}$$

$$\text{a; R=n-C}_6\text{H}_{13}, \text{ R'=n-C}_5\text{H}_{11}, \text{ b; R=MeOCH}_2, \text{ R'=MeO}$$

Ph   D
  \ /
   C=C   +   ArN₂BF₄   ——Pd(dba)₂(5 mo 1%)–MeCN,25 °C——→
  / \   86% isolated yield
 H   SiMe₃

(E)-(14)   (1d) Ar =4—NO₂C₆H₄

Ph   D   Ph   H
  \ /   \ /
   C=C   +   C=C   (4)
  / \   / \
 H   Ar   Ar   D

(E)-(15)   (Z)-(16)(89:11)

Ph   SiMe₃
  \ /
   C=C   +   ArN₂BF₄   ——Pd(dba)₂(20 mo 1%)–MeCN,25 °C——→
  / \   91% isolated yield
 H   D

(Z)-(14)   (1d)

Ph   D   Ph   D
  \ /   \ /
   C=C   +   C=C   (5)
  / \   / \
 H   Ar   Ar   H

(E)-(15)   (E)-(16)(83:17)
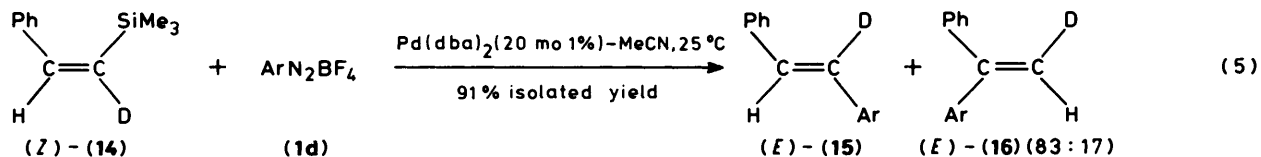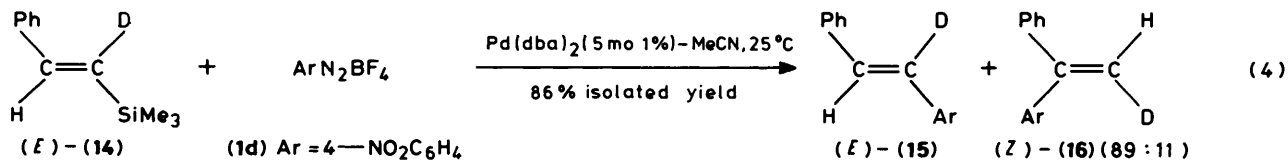
present aryldesilylation with an increase in the rate. In contrast to compound (1c), the reaction of (Z)-(4a) with compound (2c) gave a quantitative yield of arylated styrenes in the presence of only 5 mol% of Pd(dba)₂.

It was difficult to obtain pure and anhydrous crystals of ArN₂Cl (3),[11] except for 4-BrC₆H₄N₂Cl (3c) in the present study. The use of compound (3c) drastically depressed the yields and regioselectively gave the product (5c). Interestingly, (Z)-(5c) was formed with either isomer (E)- or (Z)-(4a), although the

ArN₂BF₄ + Pd(0)(dba)₂ ——→ [ArPd]⁺BF₄⁻ + N₂

yields were still very low and (E)-(5c) was the principal product. The extremely low yield in entry 23 in spite of its moderate rate suggested catalyst decay during the reaction. The decomposition products from (3c), which are well known to be unstable in anhydrous form, might deactivate the catalyst.

In the presence of a palladium(0) catalyst,[12] (E)- and (Z)-n-C₆H₁₃CH=CHSiMe₃[(E)- and (Z)-(7a)], and (E)- and (Z)-MeOCH₂CH=CHSiMe₃[(E)-and (Z)-(7b)] also reacted easily with compound (1a) to give the phenyldesilylated products (8)—(11) along with small amounts of the phenylated alkenylsilanes (12) and (13) [Equation (3) and Table 4]. The presence of allylic hydrogen may account for the formation of the isomerized products, (9) and (11). When the reactions of compound (7a) were conducted in moist acetonitrile or without exclusion of atmospheric moisture, at least 8 isomers of phenyloctene were obtained. It is possible that a protic acid, such as HBF₄, generated under moist conditions might promote the isomerization of both starting silanes and phenylated products.

Reactions of deuteriated styryltrimethylsilanes [(E)- and (Z)-(14)] with compound (1d) were employed to clarify the stereochemistry of the present aryldesilylation. Both isomers gave the same deuteriated nitrostilbene, (E)-(15), as the major product. Whereas the minor product, (Z)- or (E)-deuteriated nitrodiphenylethylene [(Z)- or (E)-(16)] was obtained stereospecifically from (E)- or (Z)-(14), respectively [Equations (4) and (5)].
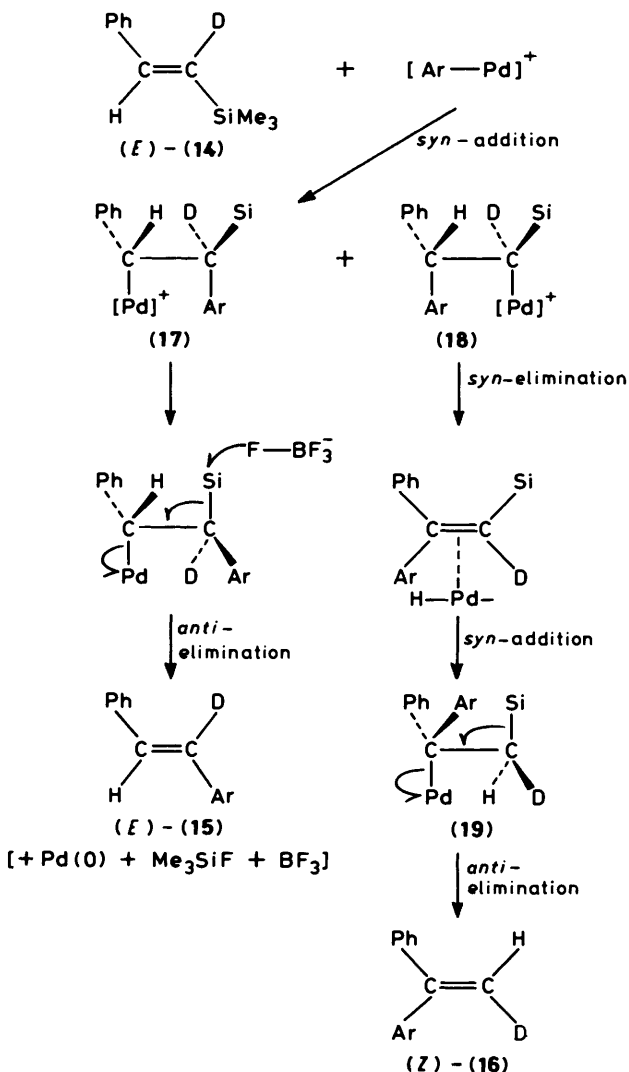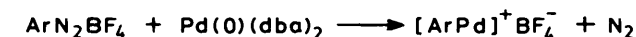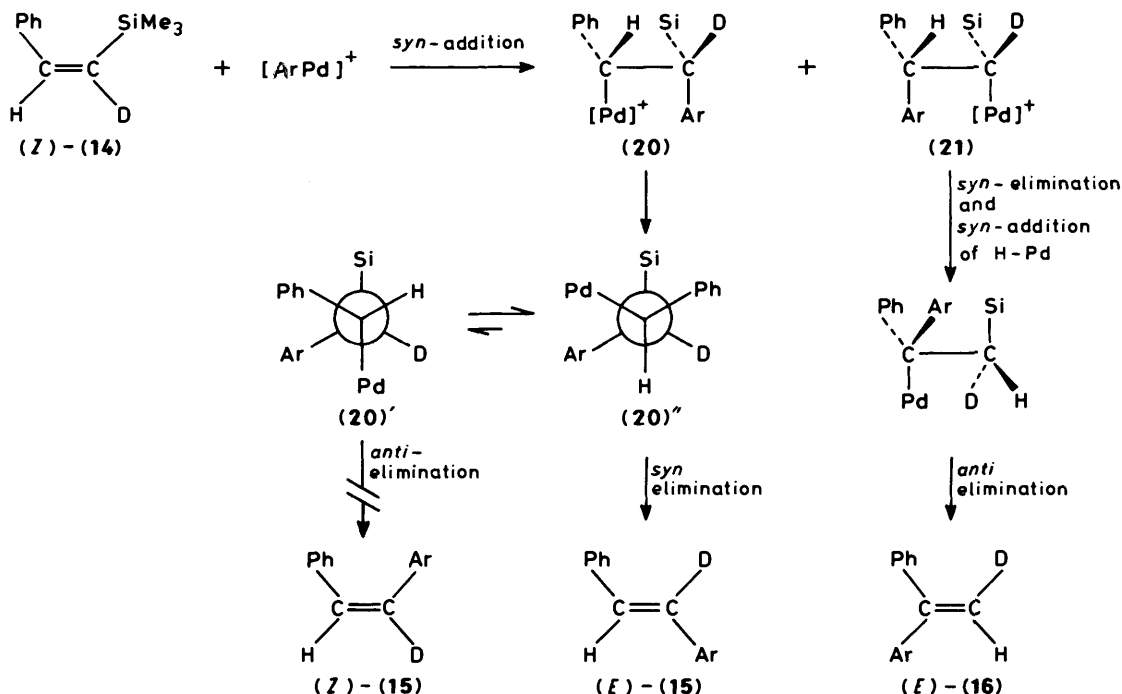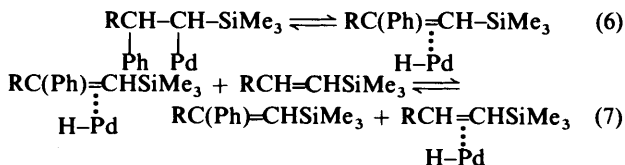
Mechanism.—Some reactions of organosilicon compounds with palladium complexes have been described as proceeding *via* a transmetallation mechanism.[4,13] However, the loss of regioselectivity in the present reaction system seems to be more compatible with an addition–elimination mechanism rather than transmetallation. Since ArPdX is known to add easily to alkenes at ambient temperature with *syn*-stereochemistry,[5,14,15] the addition of [ArPd]⁺BF₄⁻ generated from compound (1) and zero-valent palladium to alkenylsilanes can be reasonably expected as an initial step in the present aryldesilylation as shown in Schemes 1 and 2. The orientation of the addition to give compounds (17) and (18) [or (20) and (21)] determines the regiochemistry. *anti*-Elimination of Pd(0) and Me₃Si moieties from (17) gives compound (E)-(15). Such an *anti*-elimination is the most common process for organosilicons in which there is a leaving group at the β-position.[16] Zero-valent palladium is also well known to be a good leaving group in the reaction of π-allylic palladium compounds with nucleophiles.[17]

In the adducts (18) and (21) palladium should be transposed with the neighbouring carbon to undergo desilylation. The stereospecific formation of (Z)-(16) from (E)-(14), and of (E)-(16) from (Z)-(14) can be reasonably interpreted by supposing that the isomerization of compounds (18) and (21), respectively, proceeds *via syn*-elimination and re-addition of an H–Pd species followed by *anti*-elimination of Pd(0) and Me₃Si moieties as shown in Schemes 1 and 2.

The formation of the phenylated trimethylsilylalkenes (12) and (13) from compound (7) may be related to the high co-

Ph   D
  \ /
   C=C   +   [Ar—Pd]⁺
  / \
 H   SiMe₃

(E)-(14)   syn-addition

Ph H D Si   Ph H D Si
  \ | / \ /   \ | / \ /
   C——C   C——C
  /   \   /   \
[Pd]⁺   Ar   Ar   [Pd]⁺

(17)   (18)
                       |
                       syn-elimination
                       ↓

Ph H   Si   F—BF₃⁻   Ph   Si
  \ | ///   \   /
   C————C   C====C
  /| \ \   /   \
  Pd D   Ar   Ar   D
                       H—Pd–
 (Pd)

  |anti- |syn-addition
  |elimination   ↓

Ph   D   Ph Ar Si
  \ /   \ | / \
   C=C   C———C
  / \   /   \
 H   Ar   Pd H   D

(E)-(15)   (19)

[+ Pd(0) + Me₃SiF + BF₃] |anti-
                             |elimination
                             ↓

                        Ph   H
                          \   /
                           C==C
                          /   \
                         Ar   D

                        (Z)-(16)

Scheme 1.

Scheme 2.

ordinating ability of (7) to an H–Pd species [Equations (6) and (7)].[10,12]

$$RCH-CH-SiMe_3 \rightleftharpoons RC(Ph)=CH-SiMe_3 \quad (6)$$
$$\quad\quad |\quad | \qquad\qquad\qquad\qquad \vdots$$
$$\quad\quad Ph\ Pd \qquad\qquad\qquad\qquad H-Pd$$

$$RC(Ph)=CHSiMe_3 + RCH=CHSiMe_3 \rightleftharpoons$$
$$\quad\vdots \qquad\qquad\qquad\qquad\qquad$$
$$H-Pd \qquad RC(Ph)=CHSiMe_3 + RCH=CHSiMe_3 \quad (7)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \vdots$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad H-Pd$$

In the reactions of the (E)-isomers, the moderate rate retardation by the presence of a 4-nitro group on compound (1) and the drastic reduction caused by the same substituent on compound (E)-(4d) suggested that the important step is the elimination of Pd(0) from the initial adduct (17) via an E1-like pathway. The E1-like pathway is reasonable because the β-effect[18] of the silicon atom (stabilization of β-carbenium ions) is supposed to be an important factor in the anti-elimination of β-heteroatom-substituted organosilicons.[16]
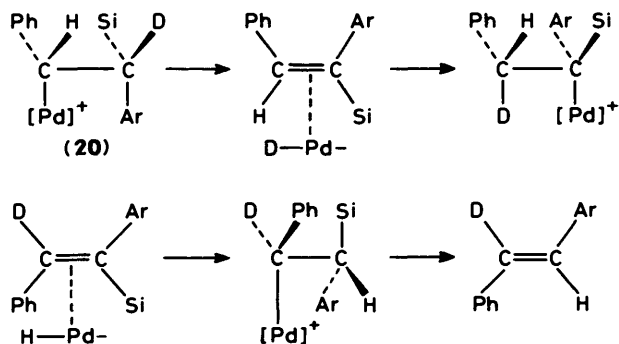
Scheme 3.

In the reaction of (Z)-isomers (Z)-(4a) and (Z)-(14), the same anti-elimination of Pd(0) and Me₃Si moieties from the initial adducts, such as (20) in Scheme 2, cannot explain the formation of the products (E)-(5) and (E)-(15). One of the possible

pathways for the unexpected stereochemistry is an isomerization of the intermediate adduct (20) via elimination and addition of DPd (or HPd) species as shown in Scheme 3. Since syn-stereochemistry of the elimination and addition of H–Pd is well documented, the isomerization process inevitably transposes deuterium from the α- to the β-carbon, and produces (E)-PhCD=CHAr. However, the n.m.r. spectrum of the (E)-stilbene derivatives from (Z)-(14) was the same as that from (E)-(14). The oxidative cleavage of (E)-(4d) by NaIO₄–OsO₄[19] gave 4-NO₂C₆H₄CHO and PhCHO with aldehyde proton resonances at 10.03 and 9.90 p.p.m., respectively, in the n.m.r. spectra. The n.m.r. spectra of the similar oxidation products of (E)-stilbene derivatives obtained from compound (Z)-(14) showed only one resonance at 9.90 p.p.m. in aldehyde proton region. Thus, it was concluded that the product from (Z)-14 was (E)-(15).

syn-Elimination of Pd(0) and Me₃Si moieties from the intermediate (20) can reasonably explain the formation of compound (E)-(5) from (Z)-(4a) and of (E)-(15) from (Z)-(14). In this case, an anti-elimination requires the more sterically congested conformer (20)'. Thus the elimination would take the syn-route via the more preferable conformer (20)". R. B. Miller and G. McGarvey have reported that the mode of elimination of Me₃SiX (X=Br, Cl) from Bu'CH(X)CH(X)SiMe₃ depends on the stability of the conformer.[20]

The contrasting effects of the substituents on compound (1) in the reactions with (E)- and (Z)-(4a) may reflect the different elimination pathways.[21]

For the present aryldesilylation, a combination of an elimination of HPdX from the initial adduct and a protodesilylation of the resulting alkenylsilane may be a possible alternative pathway [Equation (8)]. However, arylated styrylsilanes such as (Z)-(22) were not detected during the reaction. The control reactions shown in Table 5 revealed that the protodesilylation of (E)- and (Z)-PhCH=C(Ph)SiMe₃ were very slow, and gave stereospecifically compound (Z)- and (E)-(5a), respectively, although considerable isomerization was observed with increased reaction time. Consequently, the two-step mechanism could not be considered as a principal pathway in the present aryldesilylation.

Table 5. Protodesilylation of (E)- and (Z)-PhCH=CHSiMe₃[(E)- and (Z)-(22)] by HBF₄[a]

Entry	Silane (mmol)	HBF₄ (mmol)	Reaction time (min)	Conversion[b] (%)	Products, % yields[c]	
					(E)-Stilbene	(Z)-Stilbene
28	HPhC≟CPhSiMe₃ (0.02)	0.019	25	5	4	0
		0.10	122	35	28	0.3
29	HPhC≟CPhSiMe₃ (0.02)	0.019	22	9	0.8	8
		0.14	124	48	11	35

[a] Reactions were started by the addition of 42% HBF₄ to a solution of a silylated diphenylethylene in acetonitrile (0.2 ml) at 25 °C. [b] Determined by g.c. [c] g.c. yields based on the alkenylsilanes used.

$$(8)$$
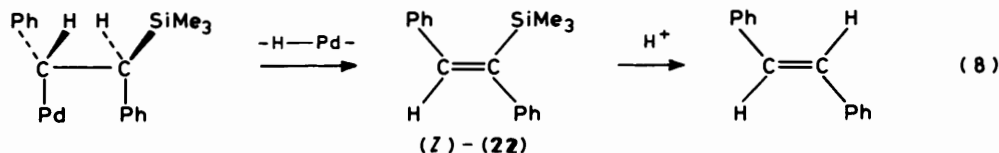
Experimental

Materials.—Acetonitrile was distilled from phosphorus pentaoxide (twice) and calcium hydride under nitrogen. Liquid arylamines were distilled before use. Guaranteed reagents of crystalline arylamines were used as received. ArN_2BF_4 (1),[22] ArN_2PF_6 (2),[23] and ArN_2Cl (3)[11] were prepared by the usual methods and stored under nitrogen at -20 °C. Pd(dba)₂ was prepared by the published method.[24] Alkenylsilanes were prepared by the following methods [Equations (9), (10), and (11)]. Their structure and purity were confirmed by n.m.r. and i.r. spectroscopy, and g.c. analysis (silicone SE-30 with FID). Isomeric purity estimated by g.c. of these alkenylsilanes was ≥99.9% except for (Z)-(4a) (96.0%) and (E)-(7b) (99.5%). The deuterium content of (E)- and (Z)-(14) estimated by n.m.r. spectroscopy was 86 and 97%, respectively. Compounds (E)- and (Z)-(25) were obtained by phenylation of (E)- and (Z)-(4a) with the Pd(OAc)₂–PPh₃ system,[15,27] respectively. Compound (E)-(25) was also prepared from PhC≡CPh by the hydrosilylation–methylation method described in Equation (9).

Aryldesilylation: General Procedure.—The reactions were started by the addition of Pd(dba)₂ to a solution of ArN₂X (0.5 mmol), an alkenylsilane (1.0 mmol), dioctyl ether (internal standard) and acetonitrile (5 ml) in a thermostatted cell (25.0 °C) equipped with a side arm and a septum cap. Gas evolution was measured by a gas burette connected to the side

arm. Samples were withdrawn at appropriate time intervals by a micro-syringe and directly analyzed on g.c. with FID. After completion of the reaction, diethyl ether (50 ml) was added. The mixture was washed with aqueous sodium carbonate and brine, and dried (anhydrous MgSO₄). After removal of solvents, the residue was chromatographed on silica gel (eluting with hexane or hexane–diethyl ether).

The structure of arylated products was determined by comparison of their n.m.r. spectra and retention times on g.c.

$$(9)^{25}$$

$$(10)^{20,26}$$

$$(11)^{15}$$

with those of authentic samples.[28] The resonances corresponding to cis- CH=CH could not be observed except for entries 20, 21, and 23 (Table 3). The formation of compound (Z)-(6c) was confirmed by comparison of its n.m.r. spectra and g.c. retention times with those of an authentic sample obtained by photochemical isomerization of compound (E)-(5c).[29] The structures of compounds (8a)—(11a) were determined by comparison of their g.c. retention times with those of authentic samples prepared by the reaction of oct-1-ene with the Pd(OAc)₂–PPh₃ system.[27] The structures of compounds (10b) and (11b) were assigned from their n.m.r. spectra: MeᵃOCH₂ᵇC(Ph)=CH₂ᶜ,ᵈ(10b), (p.p.m.), 3.39 (s, Hᵃ), 4.32 (dd, Hᵇ), 5.32 [dt, Hᶜ (Z)], 5.50 [dt, Hᵈ (E)], (J_cd 1.7, J_bc 1.7, J_bd 0.7 Hz); MeᵃOCHᵇ=C(Ph)Meᶜ (11b), 1.90 (s, Hᶜ), 3.83 s, Hᵃ), Hᵇ was obscured by the signal due to the phenyl protons. The formation of compounds (12a,b) and (13a,b) was assumed by the comparison of the g.c. retention times of the reaction

mixture components with those of the products obtained from the reactions of (E)- and (Z)-(7a,b) with PhPdOAc.[15]

Reactions of (E)- *and* (Z)-PhCH=CDSiMe₃ *with* 4-NO₂C₆H₄N₂BF₄.—The same procedure as that described above was employed with compound (E)-(14) (2.0 mmol), (1d) (1 mmol), Pd(dba)₂ (0.05 mmol), and acetonitrile (10 ml), or with (Z)-(14) (1.0 mmol), (1d) (0.5 mmol) Pd(dba)₂ (0.1 mmol), and acetonitrile (5 ml). The ordinary work-up gave an isolated yield of 86% of arylated styrenes from (E)-(14) and 91% from (Z)-(14). The isomers were separated by medium pressure chromatography (Fuji-Gel CQ-3 with CCl₄–CHCl₃ as the eluant) with u.v. detection.

The stereochemistry of the deuteriated products was confirmed by the n.m.r. spectra of their epoxides which were prepared by the reaction with perbenzoic acid in chloroform. In the following structures, Ar refers to 4-NO₂C₆H₄: (E)-PhCHᵃ–CHᵇOAr [from (E)-(5d)] δ 3.84 (d, Hᵃ), 3.94 (d, Hᵇ). (Jₐᵦ 2.64 Hz); (E)-PhCHᵃ–CODAr [from (E)-(15)] δ 3.83 (br s, Hᵃ); Ph(Ar)C=CH₂ᵃ·ᵇ (6d), δ 5.48 [d, Hᵃ (E)], 5.51 [d, Hᵇ (Z)]. (Jₐᵦ 0.93 Hz); (Z)-Ph(Ar)C=CHᵃD [(Z)-(16)] δ 5.49 (br s, Hᵃ); (E)-Ph(Ar)C=CDHᵇ δ 5.51 (br s, Hᵇ).

Reactions of (E)- *and* (Z)-PhCH=CHSiMe₃ *with* 4-Me-PhN₂BF₄ *in the presence of* (E)- *and* (Z)-PhCH=CHPh.—The reaction was started by the addition of Pd(dba)₂ (0.025 mmol) to a solution of compound (E)-(4a) (1.0 mmol) (1b) (0.5 mmol) dioctyl ether and acetonitrile (5 ml) in the presence of compound (5a) (0.14 mmol) (E:Z = 40:60) at 25 °C. The same procedure was employed in the reaction of compound (Z)-(4a) except for the use of Pd(bda)₂ (0.05 mmol) and (5a) (E:Z = 20:80) (0.60 mmol). The isomer ratio of compounds (5a) and the formation of (E)-(5b) and (6b) were monitored by g.c. In both cases the isomer ratios did not vary during the course of the reaction.

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