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Vinyl tris(trimethylsilyl)silanes: substrates for Hiyama coupling

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ABSTRACT

The oxidative treatment of vinyl tris(trimethylsilyl)silanes with hydrogen peroxide in aqueous sodium hydroxide in tetrahydrofuran generates reactive silanol or siloxane species that undergo Pd-catalyzed cross-couplings with aryl, heterocyclic, and alkenyl halides in the presence of $Pd(PPh_3)_4$ and tetrabutylammonium fluoride. Hydrogen peroxide and base are necessary for the coupling to occur while activation of the silanes with fluoride is not required. The conjugated and unconjugated tris(trimethylsilyl)silanes serve as good cross-coupling substrates. The (*E*)-silanes undergo coupling with retention of stereochemistry while coupling of (*Z*)-silanes occurred with lower stereoselectivity to produce an *E*/*Z* mixture of products.

1. Introduction

Pd-catalyzed cross-coupling reactions are a powerful method for the formation of carbon–carbon bonds under conditions that are compatible with a broad range of functional groups.[1] Among these methods, couplings between organometallics derived from group 14 metals and various electrophiles are well developed. Thus, the Stille reaction has been widely applied in modern synthetic organic chemistry.[2] Furthermore, the Hiyama coupling has received increased attention due to the lower toxicity of organosilicon compounds.[3] Procedures for coupling with organogermanes have also been reported.[4,5]

Hiyama and Hatanaka reported on the positive effect that fluoride ion imparts on the nucleophilicity of certain substituents bonded to trialkylsilanes and attributed this enhancement to the formation of pentacoordinated silicon species.[6] This strategy has opened up the door for the wide application of structurally diverse silanes including: (i) heteroatom functionalized precursors such as halosilanes, oxysilanes, silanols, and polysiloxanes and (ii) all-carbon substituted silicon species such as phenyl-, benzyl-, 2-thienyl-, 2-pyridyldimethylsilanes.[3]

Denmark et al. developed Pd-catalyzed coupling reactions employing siletanes (alkenylsilacyclobutanes) in the presence of TBAF and Pd(0) such as $Pd_2(dba)_3$.[7a] The siletanes were found to be converted in situ into reactive alkenyl(propyl)silanol and disiloxane species via the ring opening.[7b] When the alkenylsilanols were synthesized independently, they were also found to undergo coupling.[8] Hiyama, Mori et al. independently found that silver(I) oxide is an excellent activator for the coupling of alkenylsilanols with aryl iodides.[9] Generally, the organosilanols can couple by two mechanistically distinct processes. One is operative under basic conditions and requires only formation of the silanolates while the second pathway involves the use of a fluoride activator that can form an active fluorosiliconate.[10]

Recent developments in Si-cross-coupling include the application of triallyl(aryl)silanes for the synthesis of biaryls,[11a] a palladium-phosphinous acid-catalyzed and NaOH-promoted coupling of arylsiloxanes in water,[11b] application of alkenyl- and aryl[2-(hydroxymethyl)phenyl]dimethylsilanes as a reusable silicon based precursor for the fluoride-free couplings via intramolecular activation,[11c] vinylation of aryl bromides using an inexpensive vinylpolysiloxane,[11d] application of (2-pyridyl)allyldimethylsilanes as novel pyridyl transfer,[11e] and fluoride-free methodologies.[11f,g] Herein, we report application of various tris(trimethylsilyl)silanes as 'masked' substrates for the cross-coupling reactions with aryl halides and alkenyl bromides, which occurred under oxidative conditions in the presence of aqueous sodium hydroxide with or without tetrabutylammonium fluoride.

2. Results and discussion

The (*E*)-vinyl tris(trimethylsilyl)silanes (TTMS-silanes) **2a**,**c**–**f** were prepared by stereoselective radical-mediated silyl-

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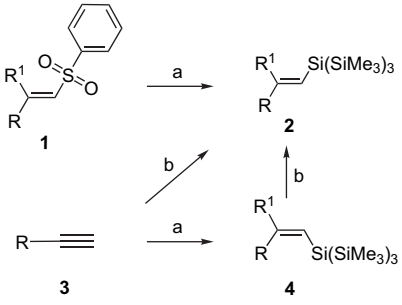
desulfonylations[5a] of the corresponding (*E*)-vinyl sulfones **1** with $(TMS)_3SiH$ (Scheme 1). The cyclohexylidene silane **2g** was similarly prepared. The (*Z*)-vinyl silanes **4a–d** were synthesized in 80–92% yield by the radical hydrosilylation[12] of the corresponding alkynes **3** with $(TMS)_3SiH$. Attempted hydrosilylation of 1-alkynes **3a–c** with $(TMS)_3SiH$ in the presence of $Rh(COD)_2BF_4/PPh_3/NaI$ or $RhCl(PPh_3)_3/NaI$ catalyst system[13] produced *E* isomers **2a–c** in high yields but complete control of stereochemistry was generally difficult since *Z* isomers **4a–c** were also formed (~5–20%). Thus, hydrosilylation of **3b** gave **2b**/**4b** (*E*/*Z*, ~9:1) mixture, which was purified to afford **2b** (82%). Isomerization (20 h, 60 °C) of the (*Z*)-silanes **4a** and **4c** with 0.5 equiv of $(TMS)_3SiH$ in the presence of Rh catalyst[13] also afforded the (*E*)-silanes **2a** (78%) and **2c** (89%). Prolonged heating (54 h) of **4b** in the presence of $(TMS)_3SiH/RhCl(PPh_3)_3/NaI$ effected quantitative conversion of **4b** into **2b**.



Series: **a** R = Ph, R^1 = H
b R = (*4*)CH_3Ph, R^1 = H
c R = (*4*)CH_3OPh, R^1 = H
d R = (*4*)CF_3Ph, R^1 = H
e R = $PhCH_2CH_2$, R^1 = H
f R = C_6H_{13}, R^1 = H
g R = R^1 = -$(CH_2)_5$-

Scheme 1. Stereoselective synthesis of (*E*)- and (*Z*)-vinyl tris(trimethylsilyl)silanes (**2** and **4**). Reagents and conditions: (a) $(Me_3Si)_3SiH$/AIBN/toluene or benzene (85 °C; oil bath); (b) $(Me_3Si)_3SiH/RhCl(PPh_3)_3$ or $Rh(COD)_2BF_4/PPh_3/NaI$/neat/Δ.

We started by examining different coupling conditions. Thus, attempted coupling of (*Z*)-vinyl silane **4b** with iodobenzene under typical coupling conditions employed for organosilanes[6] [e.g., TBAF/Pd(0)/THF] yielded the desired product **5b** in less than 5% (Table 1, entry 1). However, we found that fluoride-free treatment of **4b** with $H_2O_2/NaOH$[5a] in aqueous THF for 15 min followed by addition of iodobenzene and $Pd(PPh_3)_4$ provided (*E*/*Z*)-**5b** in 61% yield (entry 2). When NaOH was replaced with $KOSiMe_3$ base[14] the yield did not improve, although the reaction mixture became homogeneous with the combination of $KOSiMe_3/H_2O_2$ (entry 3). TBAF was found to be an excellent activator under aqueous (H_2O_2/NaOH) and 'anhydrous' ($H_2O_2/KOSiMe_3$) oxidative conditions furnishing coupling product **5b** in 90 and 81% yields, respectively (entries 4 and 5). Both peroxide and base were necessary since only 18% conversion to **5b** was obtained without NaOH or $KOSiMe_3$ (entry 6) and almost no product was formed without peroxide (entry 7). Other fluoride sources such as NaF and CsF did not show improvement over TBAF (entries 8 and 9). Anhydrous oxidative conditions [*t*-BuOOH/KH/Pd(0)] with or without TBAF did not give satisfactory results (entry 10), although such conditions worked well for the coupling of analogous TTMS-germanes.[5b] These results indicate that the peroxide and base are necessary for the coupling of TTMS-silanes to occur while fluoride facilitates this conversion (vide infra Tables 2 and 3 vs Table 4).

The protocols established above (Table 1, entries 2–5) have proven to be general for the coupling of a range of alkenyl, aryl, and heterocyclic iodides and bromides with an array of vinyl TTMS-silanes. Thus, treatment of the conjugated silane (*Z*)-**4a** with H_2O_2/H_2O (30%, 3 equiv) and NaOH (3 equiv)/H_2O in THF followed by addition of bromobenzene, $Pd(PPh_3)_4$, and TBAF gave stilbene **5a** (82%, Table 2, entry 1). Analogously, (*Z*)-**4b** coupled with iodobenzene and bromobenzene to give *p*-methylstilbene **5b** in 90 and 86% yields, respectively (entries 3 and 4). Less reactive electrophiles such as chlorobenzene and aryl triflate[15] failed to give the desired coupling products (entries 5 and 6). The substituent on the phenyl ring in (*Z*)-silanes **4a–d** (*p*-MeO, *p*-Me, H, *p*-CF_3) effects coupling reactions with bromobenzene, increasing both the yields (from 70 to 97%) and steroselectivity outcome (*E*/*Z* from 55:45 to 9:91) as the substituent changed from an electron-withdrawing group to an electron-donating group (entries 1, 4, 12, and 13). TTMS-silanes also coupled with both π-deficient (entry 2) and electron-rich heterocyclic halides (entry 9) as well as with iodonaphthalene (entry 11).

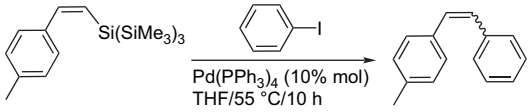
Not only aryl halides but also vinyl halides can be coupled with vinyl TTMS-silanes. Thus, oxidative treatment of (*Z*)-**4b** with β-bromostyrene produced the diene **6b** (72%, entry 7). The aliphatic 1-bromo-2-methyl-1-propene coupled with (*Z*)-**4b** yielding **7b** in high yield and high stereoselectivity (entry 8).

The (*E*)-TTMS-silanes **2a–f** underwent coupling with retention of stereochemistry. Thus, coupling of conjugated silanes **2a–d** with aryl, heterocyclic, and aliphatic bromides or iodides (H_2O_2/NaOH/Pd(0)/TBAF) provided products stereoselectively in good to excellent yields (48–90%, Table 3, entries 1–15). The electron-deficient aryl iodides gave to some extent higher yields than the electron-rich aryl iodides in the reactions with silane **2a** (entries 1, 3, and 4).

The nonconjugated (*E*)-vinyl silanes **2e–f** also undergo coupling with iodobenzene and bromobenzene under oxidative conditions in the presence of aqueous NaOH and TBAF to give the desired *E* alkenes **5e–f** (70–85%; entries 16–19). The vinyl silane **2g**, derived from cyclohexanone, successfully coupled with aryl (entries 20 and 21), alkenyl (entry 22), and heterocyclic halides (entry 23) to produce trisubstituted alkenes.

Although TBAF promotes couplings of TTMS-silanes in the presence of H_2O_2/base, we found that fluoride activation of TTMS-silanes was not necessary for the cross-coupling to occur. Thus, oxidative treatment (H_2O_2/NaOH or $KOSiMe_3$) of the conjugated silane (*E*)-**2a** with bromo- and iodobenzene also produced

Table 1
Effect of reaction parameters on the cross-coupling of TTMS-silanes

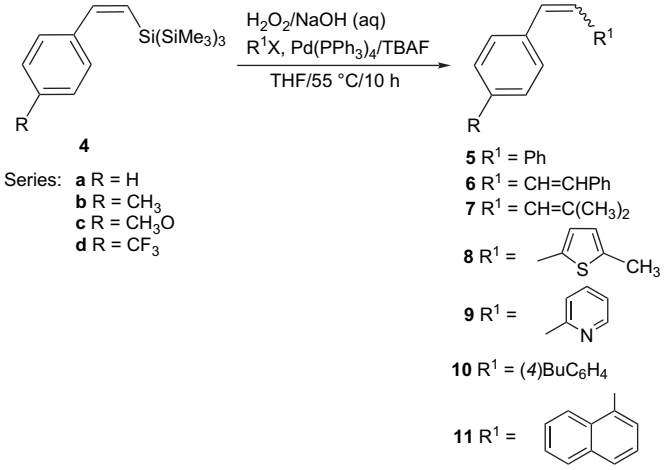


4b **5b**

Entry	Peroxide	Base	Fluoride	Yield[a] (%)	*E*/*Z*[b]
1	None	None	TBAF	<5[c]	5:95
2	H_2O_2	NaOH	None	61[d,e,f]	15:85
3	H_2O_2	$KOSiMe_3$	None	60	25:75
4	H_2O_2	NaOH	TBAF	90	3:97
5	H_2O_2	$KOSiMe_3$	TBAF	81	2:98
6	H_2O_2	None	TBAF	18[c]	67:33
7	None	$KOSiMe_3$[g]	TBAF	<2[c]	n/a
8	H_2O_2	NaOH	NaF	60	40:60
9	H_2O_2	NaOH	CsF	12[c]	60:40
10	*t*-BuOOH	KH	None[h]	15[c]	75:25

[a] Isolated yields (combined for both isomers of **5b**). Couplings were performed on 0.1 mmol scale of silane (0.03 mM).
[b] Determined by GC–MS [with internal standard of (*E*)- and (*Z*)-stilbenes] and/or ^1H NMR of the crude reaction mixture.
[c] Based on GC–MS.
[d] $Pd_2(dba)_3$ also gave **5b** (52%; *E*/*Z*, 25:75).
[e] Attempted couplings with H_2O_2 (without NaOH) or with NaOH (without H_2O_2) failed to give **5b**.
[f] Coupling with bromobenzene instead of iodobenzene gave **5b** (40%; *E*/*Z*, 20:80).
[g] Reaction with NaOH instead of $KOSiMe_3$ was also unsuccessful.
[h] Coupling in the presence of TBAF gave **5b** in ~2% yield (GC–MS).

Table 2
The coupling of vinyl (*Z*)-TTMS-silanes



4

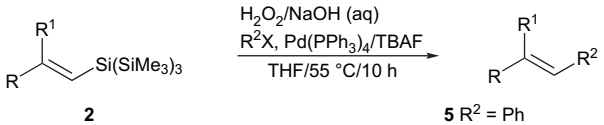
Series: **a** R = H
b R = CH_3
c R = CH_3O
d R = CF_3

5 R^1 = Ph
6 R^1 = CH=CHPh
7 R^1 = $CH=C(CH_3)_2$
8 R^1 =
9 R^1 =
10 R^1 = (*4*)BuC_6H_4
11 R^1 =

Entry	Silane	R^1X	Product	Yield[a] (%)	*E*/*Z*[b]
1	**4a**	PhBr	**5a**	82	40:60
2	**4a**	2-Iodopyridine	**9a**	60	2:98
3	**4b**	PhI	**5b**	90	3:97
4	**4b**	PhBr	**5b**	86	30:70
5	**4b**	PhCl	**5b**	<5[c]	n/a
6	**4b**	PhOTf	**5b**	<5[c]	n/a
7	**4b**	PhCH=CHBr[d]	**6b**	72	44:56[e]
8	**4b**	$(CH_3)_2C$=CHBr	**7b**	87	4:96
9	**4b**	Iodothiophene[f]	**8b**	75	15:85
10	**4b**	(*4*)BuPhI	**10b**	61	24:76
11	**4b**	1-Iodonaphthalene[g]	**11b**	73	15:85
12	**4c**	PhBr	**5c**	97	9:91
13	**4d**	PhBr	**5d**	70	55:45

[a] Isolated yields (combined for the *E*/*Z* isomers). Couplings were performed on 0.1–1.0 mmol scale of silanes (0.03 mM); $Pd(PPh_3)_4$ (10 mol %).
[b] Determined by GC–MS and/or ^1H NMR of the crude reaction mixture.
[c] GC–MS.
[d] *E*/*Z*, 88:12.
[e] 1*E*,3*E*/1*Z*,3*E*.
[f] 2-Iodo-5-methylthiophene.
[g] Coupling with 1-bromonaphthalene gave **11b** (51%, *E*/*Z*, 27:73).

Table 3
The coupling of vinyl (*E*)-TTMS-silanes



2

Series: **a** R = Ph, R^1 = H
b R = (*4*)CH_3Ph, R^1 = H
c R = (*4*)CH_3OPh, R^1 = H
d R = (*4*)CF_3Ph, R^1 = H
e R = $PhCH_2CH_2$, R^1 = H
f R = C_6H_{13}, R^1 = H
g R = R^1 = $-(CH_2)_5-$

5 R^2 = Ph
6 R^2 = CH=CHPh
7 R^2 = $CH=C(CH_3)_2$
8 R^2 =
9 R^2 =
10 R^2 = (*4*)BuC_6H_4
11 R^2 =

Entry	Silane	R^2X	Product[a] (*E*)	Yield[b] (%)
1	**2a**	PhI	**5a**	83
2	**2a**	PhBr	**5a**	67
3	**2a**	(*4*)CH_3OPhI	**5c**	79
4	**2a**	(*4*)CF_3PhI	**5d**	90
5	**2a**	$(CH_3)_2C$=CHBr	**7a**	85
6	**2a**	Iodothiophene[c]	**8a**	58
7	**2a**	2-Iodopyridine	**9a**	70
8	**2b**	PhI	**5b**	72
9	**2b**	Iodothiophene[c]	**8b**	66
10	**2b**	(*4*)BuPhI	**10b**	59
11	**2b**	1-Bromonaphthalene	**11b**	48
12	**2b**	1-Iodonaphthalene	**11b**	70
13	**2c**	PhBr	**5c**	63
14	**2c**	PhCH=CHBr[d]	**6c**[e]	60
15	**2d**	PhBr	**5d**	86
16	**2e**	PhI	**5e**	85
17	**2e**	PhBr	**5e**	72
18	**2f**	PhI	**5f**	70
19	**2f**	PhBr	**5f**	78
20	**2g**	PhI	**5g**	84
21	**2g**	PhBr	**5g**	65
22	**2g**	$(CH_3)_2C$=CHBr	**7g**	50
23	**2g**	Iodothiophene[c]	**8g**	83

[a] Only *E* isomers were detected (^1H NMR, GC–MS) except for the **g** series where stereochemistry is not relevant. Couplings were performed on 0.1–0.5 mmol scale of silanes (0.03 mM); $Pd(PPh_3)_4$ (10 mol %).
[b] Isolated yields.
[c] 2-Iodo-5-methylthiophene.
[d] *E*/*Z*, 88:12.
[e] 1*E*/3*E*.

(*E*)-stilbene (entries 1 and 2, Table 4). Other conjugated and non-conjugated (*E*)- and (*Z*)-silanes coupled with aryl, heterocyclic, and aliphatic alkenyl halides (entries 3–12). Again coupling of (*Z*)-silanes occurred with lower stereoselectivity to produce *E*/*Z* mixture (entries 9–12). It is noteworthy that TBAF containing reactions are, however, generally higher yielding and more stereoselective than the fluoride-free reactions.

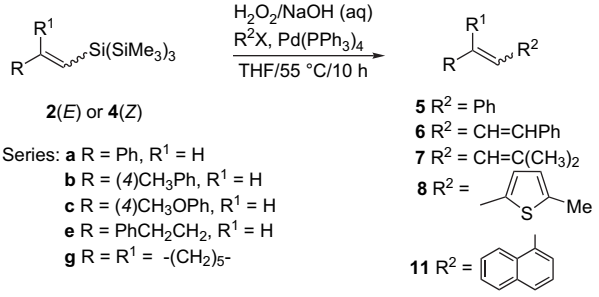
The lack of stereoselectivity for the coupling of (*Z*)-silanes probably results from the isomerization of the vinyl siloxane intermediates derived from (*Z*)-TTMS-silanes under the coupling conditions. Isomerization[16] of the products was excluded based on the following experiments: (i) no isomerization of the (*Z*)-stilbene **5a** was observed when (*Z*)-**5a** was refluxed in THF in the presence of H_2O_2/NaOH or TMSOK with or without Pd(0) and/or TBAF, (ii) coupling of the (*Z*)-silane **4b** under typical conditions [H_2O_2/NaOH/Pd(0)THF/with or without TBAF] with phenyl iodide or bromide in the presence of 0.25 or 1.0 equiv of the (*Z*)-stilbene **5a** produced product **5b** as the *E*/*Z* mixture [see Table 2 (entries 3 and 4) and Table 4 (entries 10 and 11)], while isomerization of the (*Z*)-stilbene **5a** into *E* isomer was not observed (GC–MS).

A 'side-by-side' comparison of the coupling of (*Z*)-**4b** with 1-iodonaphthalene [1 h (30%, *E*/*Z*, 0:100); 3 h (58%, *E*/*Z*, 3:97)] and 1-bromonaphthalene [1 h (22%, *E*/*Z*, 5:95); 3 h (35%, *E*/*Z*, 13:87)] showed that product **11b** is formed at different pace (Table 2, entry 11). It appears that coupling with the aryl iodides is faster and occurs with a higher degree of stereoretention than with the corresponding aryl bromides (see also Table 2, entry 3 vs 4; Table 4, entry 10 vs 11). Longer stirring of the silanes **2** and **4** with H_2O_2/NaOH (45 vs 15 min) prior to the addition of the aryl halide and the catalyst resulted in no improvement of yield and stereoselectivity.

Denmark and Tymonko have recently utilized substrates bearing two distinct silyl subunits [$RSiMe_2OH$ vs $RSiMe_2Bn$], which required complementary activations (TMSOK vs TBAF), for the construction of unsymmetrical disubstituted 1,4-butadienes.[17] TTMS-silanes can also serve as alternative organosilane substrates in Pd-catalyzed couplings. For example, TTMS-silane **2a** remained intact under typical conditions employed in the coupling of dimethylsilanols[14,17] [TMSOK(2 equiv)/$Pd_2(dba)_3$/dioxane/rt/4 h] with more than 95% of **2a** being recovered after 4 h and ~85% after 24 h. This experiment demonstrated that TTMS-silanes could act as masked silanols, which require hydrogen peroxide for initiation.

It is noteworthy that under the oxidative conditions required for coupling of TTMS-silanes, the reductive self-coupling of the halides has not been observed for the fluoride promoted reactions (Tables 2 and 3) and was only sporadically observed for the fluoride-free reactions (Table 4, entries 2, 5, and 9; 1–3%, GC–MS). Moreover,

Table 4
Fluoride-free coupling of the vinyl TTMS-silanes



Entry	Silane	R^1X	Product	Yield[a] (%)	E/Z[b]
1	**2a**	PhI	**5a**	75[c]	100:0
2	**2a**	PhBr	**5a**	50	100:0
3	**2b**	Iodothiophene[d]	**8b**	52	100:0
4	**2b**	1-Iodonaphthalene	**11b**	46	100:0
5	**2c**	PhCH=CHBr[e]	**6c**	45	100:0[f]
6	**2e**	PhI	**5e**	56	100:0
7	**2g**	PhI	**5g**	65	n/a
8	**2g**	$(CH_3)_2C$=CHBr	**7g**	42	n/a
9	**4a**	PhBr	**5a**	55	25:75
10	**4b**	PhI	**5b**	61[g]	15:85
11	**4b**	PhBr	**5b**	40[h]	20:80
12	**4b**	1-Bromonaphthalene	**11b**	30	17:83

[a] Isolated yields. Couplings were performed on 0.1 mmol scale of silanes (0.03 mM); $Pd(PPh_3)_4$ (10 mol %).
[b] Determined by ^1H NMR and/or GC–MS of the crude reaction mixture.
[c] With $KOSiMe_3$ instead of NaOH yield was 60% (*E*/*Z*, 100:0).
[d] 2-Iodo-5-methylthiophene.
[e] *E*/*Z*, 88:12.
[f] Only *E*,*E* isomer was observed.
[g] With $KOSiMe_3$ instead of NaOH yield was 60% (*E*/*Z*, 25:75).
[h] With $KOSiMe_3$ instead of NaOH yield was 48% (*E*/*Z*, 10:90).

byproducts resulting from the oxidative homocoupling[18] of the vinyl silanes **2** and **4** have not been observed. Also, although the oxidative conditions employed for generation of the active organosilane species are similar to the ones used in Tamao–Kumada and Fleming oxidation of silanes to alcohols (including vinyl silanes to aldehydes and ketones), which involve cleavage of the C–Si bond,[19] we did not observe conversion of the vinyl silanes **2** and **4** to the corresponding aldehydes. Apparently, Si–Si bond cleavage takes place chemoselectively with the C–Si bond tolerating the relatively mild oxidative conditions required for coupling.[20]

We have not yet had the opportunity to systematically investigate the mechanism(s) of the TTMS-silanes Pd-catalyzed coupling but it appears that hydrogen peroxide chemoselectively cleaves[20b] the Si–Si bond(s) to generate silanol species $RSi(OH)_n(SiMe_3)_{3-n}$ (n=1, 2, or 3). Subsequently, the silanol(s) are converted by the base to a silanolate anion, which might follow the coupling mechanism suggested by Denmark et al. for the organosilanols.[10] Alternatively, TTMS-silanes can be converted by hydrogen peroxide to siloxane species $RSi(OSiMe_3)_n(SiMe_3)_{3-n}$ (n=1, 2, or 3), that can be further transformed to the reactive pentacoordinate species (hypervalent silicate anion)[3b,e,10] by fluoride or base.

In order to obtain additional mechanistic insights, we examined the coupling reaction of **2a** with iodobenzene by ^{29}Si NMR. Thus, treatment of **2a** with hydrogen peroxide (THF-d_8/NaOH/H_2O) resulted in the appearance of new peaks at 9.82, 7.20, and 5.59 ppm, which are characteristic for the species having oxygen attached to silicon,[7b,10a,20a,b,21] with concurrent disappearance of the two distinctive peaks at −85.31 ppm (Si atom attached to sp^2 carbon) and −14.37 ppm ($SiMe_3$) for the silicon atoms present in substrate **2a**. Addition of Pd catalyst and phenyl iodide to the resulting mixture resulted in the formation of stilbene (*E*)-**5a**. Moreover, when coupling of **4b** with 1-iodonaphthalene under fluoride-free conditions was quenched after 2 h, the corresponding tris(trimethylsiloxy)silyl compound (*Z*)-**12** [(*4*)$CH_3C_6H_4CH$=$CHSi(OSiMe_3)_3$] was isolated in 7% yield in addition to product **11b** (12%). The structure of **12** was assigned based on the HRMS and NMR spectra. Subjection of **12** to TBAF promoted coupling with 1-iodonaphthalene producing product **11b** but in low yield (8%; GC–MS).

In summary, we demonstrated that the conjugated and unconjugated vinyl tris(trimethylsilyl)silanes undergo Pd-catalyzed cross-coupling with aryl, heterocyclic, and alkenyl iodides and bromides under aqueous oxidative conditions in the presence of sodium hydroxide with or without fluoride activation. Contrary to (*E*)-silanes, which undergo coupling with retention of stereochemistry, coupling of (*Z*)-silanes occurred with lower stereoselectivity giving an *E*/*Z* mixture of products. The best stereoselectivity was achieved when either aryl iodides or electron-rich TTMS-silanes were used. Under the oxidative coupling conditions neither reductive self-coupling of the halides nor oxidative homocoupling of the vinyl TTMS-silanes were observed. The tris(trimethylsilyl)silanes remained intact under typical basic conditions employed in the coupling of dimethylsilanols, thus making stable and readily accessible vinyl TTMS-silanes alternative substrates ('masked' silanols) for the Hiyama coupling. Hydrogen peroxide presumably chemoselectively cleaves Si–Si bond(s) generating active silanol/siloxane species that undergo coupling in the presence of base.

3. Experimental section

3.1. General

^1H NMR (Me_4Si) spectra at 400 or 600 MHz, ^{13}C NMR (Me_4Si) at 100.6 MHz, ^{19}F NMR (CCl_3F) at 376.4 MHz and ^{29}Si NMR (Me_4Si) at 119.2 MHz were determined with solutions in $CDCl_3$ unless otherwise noted. Mass spectra (MS) were obtained by electron ionization (EI) technique and HRMS were acquired by AP-ESI technique. Reagent grade chemicals were used and solvents were dried by reflux over CaH_2 and distillation from CaH_2 under an argon atmosphere. TLC was performed on Merck Kieselgel 60-F_{254} and products were detected with 254 nm light or by development of color with I_2. Merck Kieselgel 60 (230–400 mesh) was used for column chromatography. Purity and identity of the products (crude and/or purified) were also established using a GC–MS (EI) system with a HP 5973 mass selective detector [capillary column HP-5MS (30 m×0.25 mm×25 μm)]. The vinyl sulfones **1a**,[5a] **1c**,[22] **1e**,[5a] **1f**,[5a] **1g**[5a] and silanes **2e–g**,[5a] **4a**[12a] were prepared as reported.

3.2. (*E*)-2-(4-Methoxyphenyl)-1-[tris(trimethylsilyl)-silyl]ethene (2c)

3.2.1. Procedure A

Argon was bubbled through a solution of **1c**[22] (*E*; 150 mg, 0.55 mmol) in anhydrous benzene (10 mL) for 15 min at ambient temperature. $(Me_3Si)_3SiH$ (0.51 mL, 410 mg, 1.65 mmol) and AIBN (24 mg, 0.14 mmol) were added, and deoxygenation was continued for another 10 min. The resulting solution was refluxed at 85 °C for 4 h [additional AIBN (92 mg, 0.55 mmol) in degassed benzene (2 mL) was injected through a septum via an automatic syringe over the 4 h period or dropwise manually]. The volatiles were evaporated, and the residue was chromatographed in hexane to give **2c** (134 mg, 64%) as a colorless oil. ^1H NMR δ 0.25 (s, 27H), 3.84 (s, 3H), 6.29 (d, J=18.8 Hz, 1H), 6.87 (d, J=18.8 Hz, 1H), 6.89 (d, J=8.8 Hz, 2H), 7.35 (d, J=8.8 Hz, 2H); ^{13}C NMR δ 1.0, 55.4, 114.0, 119.6, 127.2, 132.4, 145.0, 159.3; MS (EI) m/z 380 (15, M^+), 174 (100). AP-ESI-HRMS calcd for $C_{18}H_{36}ONaSi_4$ (MNa^+): 403.1735. Found: 403.1739.

Treatment of **4c** (381 mg, 1 mmol) with $(Me_3Si)_3SiH$ (0.15 mL, 124 mg, 0.5 mmol) in the presence of Rh catalyst, as described for **2a** [GC–MS of the crude reaction mixture: **2c**/**4c** (*E*/*Z*, 92:8; t_R 22.02 min, *Z*; t_R 22.34 min, *E*)], gave **2c** (338 mg, 89%).

3.3. (*Z*)-2-(4-Methylphenyl)-1-[tris(trimethylsilyl)-silyl]ethene (4b)

3.3.1. Procedure B

$(Me_3Si)_3SiH$ (0.31 mL, 248 mg, 1 mmol) was added in one portion via a syringe to a degassed solution of **3b** (0.13 mL, 116 mg, 1 mmol) in dry benzene (3 mL) at ambient temperature under nitrogen atmosphere. AIBN (83.8 mg, 0.50 mmol) was then added and the resulting solution was heated (oil bath, 85 °C) for 3 h or until the alkyne was consumed (GC). The volatiles were evaporated in vacuo and the oily residue was flash chromatographed (hexane) on silica gel to give **4b** (336 mg, 92%) as a colorless oil. ^{1}H NMR δ 0.16 (s, 27H), 2.37 (s, 3H), 5.82 (d, J=14.5 Hz, 1H), 7.16 (d, J=7.8 Hz, 2H), 7.22 (d, J=7.8 Hz, 2H), 7.40 (d, J=14.5 Hz, 1H); ^{13}C NMR δ 1.4, 21.3, 123.1, 128.1, 129.0, 137.1, 137.8, 146.6; ^{29}Si NMR δ −88.33 [s, *Si*($SiMe_3$)$_3$], −11.67 [s, Si(*Si*Me_3)$_3$]; GC–MS: (t_R 22.12 min) m/z 364 (6, M^+), 174 (100). HRMS calcd for $C_{18}H_{36}Si_4$ (M^+): 364.1894. Found: 364.1896.

3.4. (*E*)-1,2-Diphenylethene (5a)

3.4.1. Procedure C

Solution of NaOH (60 mg, 1.5 mmol) and H_2O_2 (30% solution, 0.15 mL, 1.5 mmol) in deionized H_2O (1.5 mL) was added to a stirred solution of **2a** (175 mg, 0.5 mmol) in THF (15 mL) at ambient temperature. After 15 min, iodobenzene (84 μL, 153 mg, 0.75 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and tetrabutylammonium fluoride (1 M/THF, 1.5 mL, 1.5 mmol) were added and the resulting brownish mixture was heated at 55 °C (oil bath) for 10 h. The volatiles were evaporated and the residue was partitioned (H_2O/$CHCl_3$). The aliquot of the organic layer was subjected to GC–MS and/or ^{1}H NMR analysis in order to establish the overall stereochemistry. The organic layer was dried ($MgSO_4$), evaporated, and column chromatographed (hexane) to give (*E*)-**5a** (74 mg, 83%) with data identical to commercial sample; GC–MS (t_R 17.9 min, *E*) m/z 180 (100, M^+).

Treatment of **2a** (35 mg, 0.10 mmol) with bromobenzene (16 μL, 23.6 mg, 0.15 mmol) by procedure C gave (*E*)-**5a** (12 mg, 67%).

Analogous treatment of **2a** (35 mg, 0.10 mmol) with iodobenzene (17 μL, 31 mg, 0.15 mmol) by procedure C (without TBAF) gave (*E*)-**5a** (13.5 mg, 75%).

Analogous treatment of **2a** (35 mg, 0.10 mmol) with bromobenzene (16 μL, 23.6 mg, 0.15 mmol) by procedure C (without TBAF) gave (*E*)-**5a** (9 mg, 50%). Also, biphenyl (1%; e.g., 2% consumption of bromobenzene) was detected; GC–MS (t_R 11.3 min) m/z 154 (100, M^+).

3.4.2. Procedure D

$KOSiMe_3$ (38.5 mg, 0.3 mmol) and H_2O_2 (30% solution, 31 μL, 0.30 mmol) were added to a stirred solution of **2a** (35 mg, 0.10 mmol) in THF (3 mL) at ambient temperature. After 20 min, iodobenzene (17 μL, 31 mg, 0.15 mmol) and $Pd(PPh_3)_4$ (11 mg, 0.01 mmol) were added and the resulting mixture was heated at 55 °C (oil bath) for 10 h. Aqueous work-up and purification as described in procedure C gave (*E*)-**5a** (11 mg, 60%).

3.5. (*E*/*Z*)-1,2-Diphenylethene (5a)

Treatment of **4a**[12a] (35 mg, 0.10 mmol) with bromobenzene (16 μL, 23.6 mg, 0.15 mmol) by procedure C gave **5a** (*E*/*Z*, 40:60; 15 mg, 82%) with data identical to commercial sample; GC–MS (t_R 15.1 min, Z; t_R 17.9 min, *E*) m/z 180 (100, M^+). HRMS calcd for $C_{14}H_{13}$ (MH^+): 181.1073. Found: 181.1079.

Analogous treatment of **4a** (35 mg, 0.10 mmol) with bromobenzene (16 μL, 23.6 mg, 0.15 mmol) by procedure C (without TBAF) gave **5a** (*E*/*Z*, 25:75; 10 mg, 55%). Also, biphenyl (3%; e.g., 6% consumption of bromobenzene) was detected (GC–MS).

3.6. (*E*)-1-(4-Methylphenyl)-2-phenylethene (5b)

Treatment of **2b** (36.5 mg, 0.10 mmol) with iodobenzene (17 μL, 31 mg, 0.15 mmol) by procedure C gave (*E*)-**5b** (14 mg, 72%) with data as reported.[23] ^{1}H NMR δ 2.22 (s, 3H), 6.92 (d, J=18.1 Hz, 1H), 6.98 (d, J=18.1 Hz, 1H), 7.03 (d, J=7.9 Hz, 2H), 7.13 (t, J=7.3 Hz, 1H), 7.22 (t, J=7.4 Hz, 2H), 7.30 (d, J=8.1 Hz, 2H), 7.39 (d, J=7.9 Hz, 2H); GC–MS (t_R 19.6 min) m/z 194 (100, M^+).

3.7. (*E*/*Z*)-1-(4-Methylphenyl)-2-phenylethene (5b)

Treatment of **4b** (364 mg, 1.0 mmol) with iodobenzene (0.17 mL, 306 mg, 1.5 mmol) by procedure C gave **5b**[23b] (*E*/*Z*, 3:97; 175 mg, 90%); GC–MS (t_R 16.8 min, *Z*; t_R 19.6 min, *E*) m/z 194 (100, M^+). HRMS calcd for $C_{15}H_{15}$ (MH^+): 195.1174. Found: 195.1179. (*Z*)-**5b** had: ^{1}H NMR δ 2.20 (s, 3H), 6.43 (s, 2H), 6.92 (d, J=7.9 Hz, 2H), 7.03 (d, J=7.9 Hz, 2H), 7.11–7.20 (m, 5H).

Treatment of **4b** (36.5 mg, 0.10 mmol) with bromobenzene (16 μL, 23.6 mg, 0.15 mmol) by procedure C gave **5b** (*E*/*Z*, 30:70; 17 mg, 86%).

Analogous treatment of **4b** (36.5 mg, 0.10 mmol) with iodobenzene (17 μL, 31 mg, 0.15 mmol) by procedure C (without TBAF) gave **5b** (*E*/*Z*, 15:85; 12 mg, 61%). Identical coupling with bromobenzene (0.15 mmol) gave **5b** (*E*/*Z*, 20:80; 8 mg, 40%).

Treatment of **4b** (36.5 mg, 0.10 mmol) with iodobenzene (17 μL, 31 mg, 0.15 mmol) by procedure D gave **5b** (*E*/*Z*, 25:75; 11.6 mg, 60%). Identical coupling with bromobenzene (0.15 mmol) gave **5b** (*E*/*Z*, 10:90; 9 mg, 48%).

Analogous treatment of **4b** (36.5 mg, 0.10 mmol) with iodobenzene (17 μL, 31 mg, 0.15 mmol) by procedure D [with addition of TBAF (0.3 mmol) as described in procedure C] gave **5b** (*E*/*Z*, 2:98; 15.7 mg, 81%).

Analogous treatment of **4b** (36.5 mg, 0.10 mmol) with iodobenzene by procedure C [using aqueous NaF (12.6 mg, 0.3 mmol) instead of TBAF] gave **5b** (*E*/*Z*, 40:60; 11.6 mg, 60%).

Analogous treatment of **4b** (36.5 mg, 0.10 mmol) with iodobenzene by procedure C [using $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol) instead of $Pd(PPh_3)_4$ and without addition of TBAF] gave **5b** (*E*/*Z*, 25:75; 10 mg, 52%).

3.8. (*Z*)-2-(4-Methylphenyl)-1-[tris(trimethylsiloxy)-silyl]ethene (12)

Treatment of **4b** (50 mg, 0.14 mmol) with 1-iodonaphthalene (22 μL, 35 mg, 0.14 mmol) by procedure C [without TBAF, 2 h, NaOH (5 equiv)] and column chromatography (hexane) gave **12** (4 mg, 7%) and **11b** (*E*/*Z*, 7:93; 4 mg, 12%). Compound **12** had: ^{1}H NMR δ 0.07 (br s, 27H), 2.36 (s, 3H), 5.50 (d, J=15.5 Hz, 1H), 7.12 (d, J=7.9 Hz, 2H), 7.21 (d, J=15.5 Hz, 1H) 7.44 (d, J=8.0 Hz, 2H); GC–MS (t_R 17.60 min) m/z 412 (6, M^+), 175 (100). HRMS calcd for $C_{18}H_{37}O_3Si_4$ (MH^+): 413.1814. Found: 413.1823.

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Supplementary data

Experimental procedures and characterization data for compounds **1d**, **2a**, **2b**, **2d**, **4c**, **4d**, **5c**–**g**, **6b**, **6c**, **7a**, **7b**, **7g**, **8a**, **8b**, **8g**, **9a**, **10b**, and **11b**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.03.024.

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