

# Highly Stereospecific, Palladium-Catalyzed Cross-Coupling of Alkenylsilanols

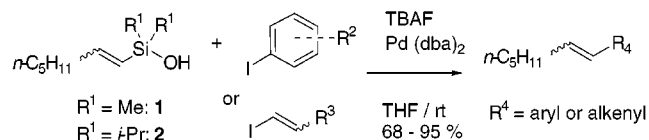
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## ABSTRACT



Alkenylsilanols bearing methyl ((*E*-1 and (*Z*-1) or isopropyl ((*E*-2 and (*Z*-2) substituents are converted to disubstituted alkenes by a palladium-(0)-catalyzed cross-coupling reaction with aryl or vinyl iodides in the presence of tetrabutylammonium fluoride or hydroxide. Yields and stereoselectivities are generally high, and the reaction is compatible with a wide range of functional groups.

The importance of metal-catalyzed, cross-coupling reactions for the construction of carbon–carbon bonds between unsaturated centers is unparalleled. The extraordinary diversity of organometallic nucleophiles and organic electrophiles that have been enlisted into useful service is testimony to the continuing interest in identifying milder procedures and broader structural generality for this transformation.<sup>1</sup> Of paramount importance in developing new cross-coupling reactions are the following: (1) ease of preparation of the organic “donor”, (2) mildness of reaction conditions, (3) stereospecificity, (4) functional group compatibility, and (5) tractability of byproducts.

While organosilicon compounds could, in principle, represent ideal coupling partners, only in recent years have practical procedures been developed that address, in part, the invention criteria outlined above. Among the most notable are aryl- and/or alkenylfluorosilanes,<sup>2</sup> -fluorosiliconates,<sup>3a</sup> and -orthosiliconates.<sup>3b</sup> In two recent reports from this laboratory,

(1) (a) Diederich, F., Stang, P. J., Eds. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, 1998. (b) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (c) Tsuji, I. *Palladium Reagents and Catalysts. Innovations in Organic Synthesis*; Wiley: Chichester, U.K., 1995.

(2) (a) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845. (b) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; Chapter 10. (c) Horn, K. A. *Chem. Rev.* **1995**, 95, 1317.

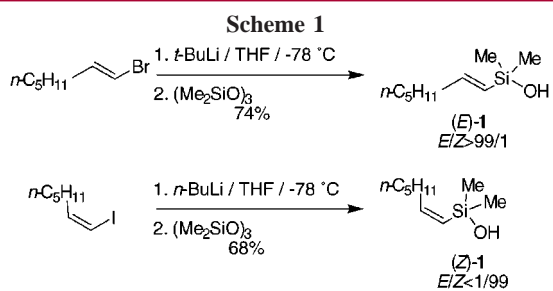
the utility of alkenyl- and arylsilacyclobutanes for mild and stereospecific cross-coupling reactions has been documented.<sup>4</sup> These agents demonstrate significant practical advantages when compared to other silicon-based methods in ease of preparation, mildness of reaction conditions, and stereospecificity.

As part of our continuing efforts to identify other simple silicon derivatives capable of engaging in mild cross-coupling processes, we have found that silanols and disiloxanes are also competent in effecting this transformation under conditions nearly identical to those employed for the alkenylsilacyclobutanes.<sup>5</sup> In this Letter, we disclose the preparation and cross-coupling of geometrically defined alkenylsilanols with a variety of aryl and alkenyl iodides.<sup>6</sup>

To make direct comparisons to the previously described cross-coupling with alkenylsilacyclobutanes, we chose to examine the geometrically defined (1-heptenyl)-dimethylsilanols (*E*-1 and (*Z*-1 and (1-heptenyl)-di(isopropyl)silanols (*E*-2 and (*Z*-2). These substrates could be easily prepared by following established procedures as outlined in Schemes 1 and 2.<sup>5b,7</sup> Thus, treatment of (*E*-1-bromo-1-heptene<sup>8</sup> with

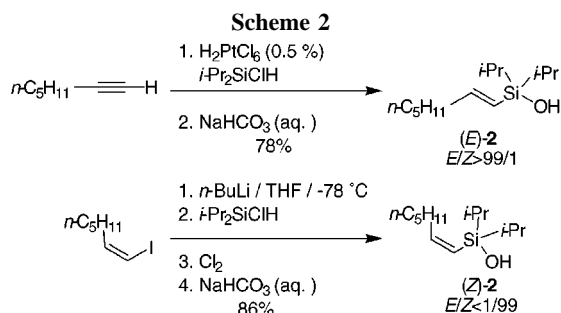
(3) (a) Mowery, M. E.; DeShong, P. J. *Org. Chem.* **1999**, 64, 3266. (b) Mowery, M. E.; DeShong, P. J. *Org. Chem.* **1999**, 64, 1684.

(4) (a) Denmark, S. E.; Choi, J. Y. *J. Am. Chem. Soc.* **1999**, 121, 5821. (b) Denmark, S. E.; Wu, Z. *Org. Lett.* **1999**, 1, 1495.



*tert*-butyllithium, followed by the addition of hexamethylcyclotrisiloxane, resulted in the formation of (*E*)-**1** in 74% yield. The corresponding *Z*-isomer was prepared in a similar manner from (*Z*)-1-iodo-1-heptene<sup>9</sup> which upon treatment with *n*-butyllithium and hexamethylcyclotrisiloxane afforded (*Z*)-**1** in 68% yield.<sup>10</sup>

To investigate the influence of the nontransferable groups on the silicon atom (and illustrate an alternative entry to the silanol precursors), we also prepared di(isopropyl)silanols (*E*)-**2** and (*Z*)-**2** (Scheme 2). Catalytic ( $\text{H}_2\text{PtCl}_6$ ) hydrosily-



lation of 1-heptyne with chlorodi(isopropyl)silane followed by alkaline hydrolysis provided (*E*)-**2** in 78% yield.<sup>10,11</sup> The

(5) For recent reports on the preparation and synthetic transformations of silanols, see: (a) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147. (b) Hirabayashi, K.; Takahisa, E.; Nishihara, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2409. (c) Hirabayashi, K.; Nishihara, Y.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 7893. (d) Chan, T. H.; Chen, L. M.; Wang, D. J. *Chem. Soc., Chem. Commun.* **1988**, 1280. (e) Chan, T. H.; Chen, L. M.; Wang, D.; Li, L. H. *Can. J. Chem.* **1993**, *71*, 60. (f) Yamamoto, K.; Kawanami, Y.; Miyazawa, M. *J. Chem. Soc., Chem. Commun.* **1993**, 436. (g) Li, L. H.; Chan, T. H. *Tetrahedron Lett.* **1997**, *38*, 101. (h) Takaku, K.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* **1996**, *37*, 6781. (i) Takaku, K.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* **1997**, *38*, 5189. (j) Uehara, S.; Takaku, H.; Shinokubo, K.; Oshima, K. *Synlett* **1998**, 1096. (k) Trost, B. M.; Ito, N.; Greenspan, P. D. *Tetrahedron Lett.* **1993**, *34*, 1421. (l) Soderquist, J. A.; Vaquer, J.; Diaz, M. J.; Rane, A. M.; Bordwell, F. G.; Zhang, S. *Tetrahedron Lett.* **1996**, *37*, 2561. (m) Akiyama, T.; Imazeki, S. *Chem. Lett.* **1997**, 1077.

(6) Hiyama has recently described the palladium-catalyzed cross-coupling of aryl- and (*E*)-alkenylsilanol with aryl halides in the presence of 200 mol % of silver(I) oxide. These reactions required 36 h at 60 °C and may also be mechanistically distinct from the couplings described herein. Hirabayashi, K.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. *Org. Lett.* **1999**, *1*, 299.

(7) (a) Sieburth, S. McN.; Mu, W. *J. Org. Chem.* **1993**, *58*, 6314. (b) Sieburth, S. McN.; Fensterbank, L. *J. Org. Chem.* **1993**, *58*, 7584.

(8) Kropp, P. J.; Crawford, S. D. *J. Org. Chem.* **1994**, *59*, 3102.

(9) Ravid, U.; Silverstein, R. M.; Smith, L. R. *Tetrahedron* **1978**, *34*, 1449.

stereoisomer (*Z*)-**2** was produced by a high-yielding, three-step synthesis starting from (*Z*)-1-iodo-1-heptene.<sup>9</sup> Lithium–iodide exchange with *n*-butyllithium, followed by the addition of chlorodi(isopropyl)silane, formed the intermediate (1-heptenyl)di(isopropyl)silane in 95% yield. Oxidation with chlorine (0.9 M solution in  $\text{CCl}_4$ ), followed by mild hydrolysis, produced (*Z*)-**2** in 90% yield over two steps.<sup>10</sup>

With the requisite silanols in hand, we next investigated their ability to undergo palladium(0) catalyzed cross-couplings. The extensive optimization of reaction conditions (palladium catalyst, fluoride source, stoichiometry, solvent, and temperature) already carried out in the context of the silacyclobutane coupling provided an ideal starting point for these studies. Accordingly, the silanol was first combined with tetrabutylammonium fluoride (TBAF) in THF for 10 min at room temperature, followed by the addition of the organic iodide and the palladium complex ( $\text{Pd}(\text{dba})_2$ ). We were delighted to discover that the reactions were generally complete within 10–30 min (Table 1). Again following the lessons from previous studies, the product was separated from, *inter alia*, polysilicone byproducts by a three-step procedure: (1) filtration of the reaction mixture through a plug of silica gel, (2) column chromatography (silica gel or reverse phase C18), and (3) distillation. These conditions differ from those employed for silacyclobutanes only in the amount of TBAF added. It was shown that only 2 equiv of a freshly prepared TBAF solution was enough to effectively promote the cross-coupling of silanols within 10 min.

With silacyclobutanes it was observed that the reactions stalled at ca. 85% conversion when less than 3 equiv of a commercially available THF solution of TBAF (1 M) was used; however, this was later found to be dependent on the quality of the TBAF employed.<sup>12</sup> Further reduction in the amount the TBAF, however, resulted in a decrease in the reaction rate and yield (cf. entries 8 and 9 in Table 1).

The fluoride is required, however, as omission of TBAF from the reaction mixtures resulted in complete recovery of both the aryl iodide and the silanol.<sup>13</sup>

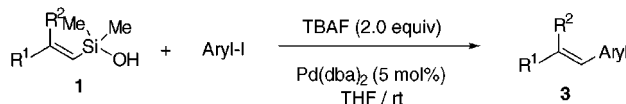
We have discovered that while a basic/nucleophilic activator is essential, it need not be fluoride. Substitution of tetrabutylammonium fluoride with the hydroxide (as a 2.0 M solution in methanol) gave rise to a comparable rate and yield for the coupling of (*E*)-**1** with 1-iodonaphthalene (cf. entries 3 and 5, Table 1). However, the product is accompanied by 2.5% of the cine rearrangement product.

The similarity in rate and yield for the cross-coupling of silacyclobutanes and dimethylsilanols was indeed satisfying. Selectivities obtained with the dimethylsilanols were slightly lower than those observed with the silacyclobutanes; up to

(10) Silanols (*E*)- and (*Z*)-**1** and (*E*)- and (*Z*)-**2** were all obtained in geometrically pure form (>99%), as established by capillary GC analysis. (11) Miller, R. B.; McGarvey, G. J. *Org. Chem.* **1978**, *43*, 4424.

(12) 1 M TBAF solutions were prepared from commercially available crystalline TBAF and freshly distilled THF. Analysis by <sup>19</sup>F NMR spectroscopy showed one single signal at –115.9 ppm (vs  $\text{CFCl}_3$ ). The commercially available 1 M solution contained more than five different signals in the <sup>19</sup>F NMR spectrum. Silacyclobutanes could be cross-coupled in high yields and conversions, using only 2 equiv of the freshly prepared TBAF solution.

(13) The silanol is partly converted into the disiloxane during isolation; however mass balance accounts for 93% of the initially employed silanol.

**Table 1.** Palladium-Catalyzed Cross-Coupling of (*E*)-**1** and (*Z*)-**1** with Aryl Iodides<sup>a</sup>

entry	silane	R <sup>1</sup>	R <sup>2</sup>	aryl	time, min	product	yield, <sup>b</sup> %	ratio, <sup>c</sup> <i>E</i> / <i>Z</i>
1	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	C <sub>6</sub> H <sub>5</sub>	10	( <i>E</i> )- <b>3a</b>	91	97.8/2.2
2	( <i>Z</i> )- <b>1</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	10	( <i>Z</i> )- <b>3a</b>	90	2.7/97.3
3	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	1-naphthyl	30	( <i>E</i> )- <b>3b</b>	89	96.5/3.5
4	( <i>Z</i> )- <b>1</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	1-naphthyl	30	( <i>Z</i> )- <b>3b</b>	85	3.3/96.7
5 <sup>d</sup>	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	1-naphthyl	30	( <i>E</i> )- <b>3b</b>	76	96.6/3.4 (2.5% cine)
6 <sup>e</sup>	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	2-thienyl	180	( <i>E</i> )- <b>3c</b>	83	95.7/4.3
7 <sup>e</sup>	( <i>Z</i> )- <b>1</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	2-thienyl	180	( <i>Z</i> )- <b>3c</b>	81	2.5/97.5
8	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	4-(CH <sub>3</sub> CO)C <sub>6</sub> H <sub>4</sub>	10	( <i>E</i> )- <b>3d</b>	93	96.5/3.5
9 <sup>f</sup>	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	4-(CH <sub>3</sub> CO)C <sub>6</sub> H <sub>4</sub>	60	( <i>E</i> )- <b>3d</b>	87	95.5/4.5
10 <sup>g</sup>	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	4-(CH <sub>3</sub> CO)C <sub>6</sub> H <sub>4</sub>	180	( <i>E</i> )- <b>3d</b>	74	96.9/3.1
11	( <i>Z</i> )- <b>1</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	4-(CH <sub>3</sub> CO)C <sub>6</sub> H <sub>4</sub>	10	( <i>Z</i> )- <b>3d</b>	92	4.8/95.2
12	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	4-(CH <sub>3</sub> O)C <sub>6</sub> H <sub>4</sub>	10	( <i>E</i> )- <b>3e</b>	95	97.2/2.8
13	( <i>Z</i> )- <b>1</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	4-(CH <sub>3</sub> O)C <sub>6</sub> H <sub>4</sub>	10	( <i>Z</i> )- <b>3e</b>	94	2.6/97.4

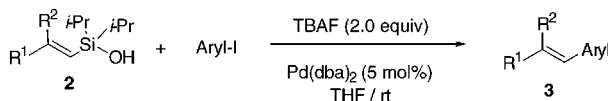
<sup>a</sup> All reactions employed 1.1 equiv of **1** unless otherwise noted. <sup>b</sup> Yield of chromatographically homogeneous materials. <sup>c</sup> Determined by GC analysis. <sup>d</sup> 2.0 equiv of tetrabutylammonium hydroxide (2.0 M solution in CH<sub>3</sub>OH) was employed. <sup>e</sup> 1.2 equiv of **1** used. <sup>f</sup> 1.0 equiv of TBAF was used. <sup>g</sup> 1.2 equiv of **1** and 2.5 mol % of [allylPdCl<sub>2</sub>] were used with 4-bromoacetophenone; after 2 h, an additional equivalent of TBAF and 1.25 mol % of [allylPdCl<sub>2</sub>] were added.

5.5% of the geometrical isomer was observed, starting from a single, pure isomer of the (*E*)- or (*Z*)-silanol.

Accordingly, the influence of the nontransferable group on the rate and specificity of the coupling was studied by submitting the diisopropylsilanols ((*E*)- and (*Z*)-**2**) to the coupling reaction conditions. The results summarized in Table 2 show clearly that the rates for the cross-coupling are independent of the substituents on the silicon atom. However, the selectivity of the reaction is now comparable to the selectivity observed with silacyclobutane and substantially improved over the selectivity obtained with the dimethylsilanols (for example, cf. Table 1, entries 1 and 2, and Table 2, entries 1 and 2). Moreover, when tetrabutylammonium hydroxide was used as the activator (cf. Table 1, entry 5, and Table 2, entry 5), no cine rearrangement product was observed.

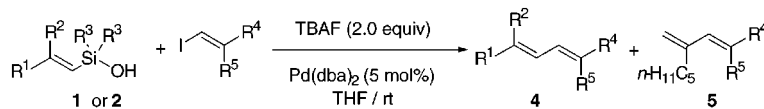
The experiments described in Table 1 clearly demonstrate that the influence of the different functional groups present on the aryl iodide is minimal. The rate and yield of the reactions are not affected, and the presence of electronically neutral (entries 1–5), donating (entries 10 and 11), and withdrawing (entries 8 and 9) substituents is well tolerated.

As was the case with alkenylsilacyclobutanes, silanols (*E*)-**1** and (*Z*)-**1** undergo rapid and specific cross-coupling with alkenyl iodides as well. For this study, geometrically isomeric electrophiles (*E*)- and (*Z*)-6-iodo-5-hexenols were employed (Table 3). Under conditions identical to those employed previously, the vinyl iodides reacted with the silanols to give conjugated dienes **4** in good yield. The reactions were generally slower than the coupling reactions with aryl iodides. In all cases, the desired products were contaminated with a small and variable amount of isomeric

**Table 2.** Palladium-Catalyzed Cross-Coupling of (*E*)-**2** and (*Z*)-**2** with Aryl Iodides<sup>a</sup>

entry	silane	R <sup>1</sup>	R <sup>2</sup>	aryl	time, min	product	yield, <sup>b</sup> %	ratio, <sup>c</sup> <i>E</i> / <i>Z</i>
1	( <i>E</i> )- <b>2</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	C <sub>6</sub> H <sub>5</sub>	10	( <i>E</i> )- <b>3a</b>	82	99.2/0.8
2	( <i>Z</i> )- <b>2</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	10	( <i>Z</i> )- <b>3a</b>	81	0.6/99.4
3	( <i>E</i> )- <b>2</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	1-naphthyl	30	( <i>E</i> )- <b>3b</b>	85	98.4/1.6
4	( <i>Z</i> )- <b>2</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	1-naphthyl	30	( <i>Z</i> )- <b>3b</b>	79	2.3/97.7
5	( <i>E</i> )- <b>2</b> <sup>d</sup>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	1-naphthyl	30	( <i>E</i> )- <b>3b</b>	78	99.2/0.8
6	( <i>E</i> )- <b>2</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	4-(CH <sub>3</sub> CO)C <sub>6</sub> H <sub>4</sub>	10	( <i>E</i> )- <b>3d</b>	80	>99.5/0.5
7	( <i>Z</i> )- <b>2</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	4-(CH <sub>3</sub> CO)C <sub>6</sub> H <sub>4</sub>	10	( <i>Z</i> )- <b>3d</b>	86	1.0/99.0

<sup>a</sup> All reactions employed 1.1 equiv of **2**. <sup>b</sup> Yield of chromatographically homogeneous materials. <sup>c</sup> Determined by GC analysis. <sup>d</sup> 2.0 equiv of tetrabutylammonium hydroxide was used instead of TBAF.

**Table 3.** Palladium-Catalyzed Cross-Coupling of (*E*)-**1** and (*Z*)-**1** Alkenyl Iodides<sup>a</sup>

entry	silane	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	time, min	product	yield, <sup>b</sup> %	ratios <sup>c,d</sup>	ratio <sup>d</sup> 4/5
1	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	Me	(CH <sub>2</sub> ) <sub>4</sub> OH	H	90	( <i>E,E</i> )- <b>4</b>	91	95.8/4.2 <sup>f</sup>	86/14
2	( <i>E</i> )- <b>2</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	<i>i</i> -Pr	(CH <sub>2</sub> ) <sub>4</sub> OH	H	90	( <i>E,E</i> )- <b>4</b>	87	97.8/2.2	96/4
3	( <i>Z</i> )- <b>1</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	Me	(CH <sub>2</sub> ) <sub>4</sub> OH	H	90	( <i>E,Z</i> )- <b>4</b>	72	95.4/4.6 <sup>g</sup>	91/9
4	( <i>E</i> )- <b>1</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	Me	H	(CH <sub>2</sub> ) <sub>4</sub> OH	90	( <i>Z,E</i> )- <b>4</b>	73	5.9/94.1	>99/1
5 <sup>e</sup>	( <i>Z</i> )- <b>1</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	Me	H	(CH <sub>2</sub> ) <sub>4</sub> OH	300	( <i>Z,Z</i> )- <b>4</b>	64	12.2/87.8 <sup>h</sup>	>99/1
6 <sup>e</sup>	( <i>Z</i> )- <b>2</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<i>i</i> -Pr	H	(CH <sub>2</sub> ) <sub>4</sub> OH	300	( <i>Z,Z</i> )- <b>4</b>	68	7.6/92.4 <sup>h</sup>	93.2/6.8

<sup>a</sup> All reactions employed 1.1 equiv of **1** and 5 mol % Pd(dba)<sub>2</sub> unless otherwise noted. <sup>b</sup> Yield of chromatographically pure materials. <sup>c</sup> Isomeric purity of major component. <sup>d</sup> Determined by GC analysis. <sup>e</sup> 1.5 equiv of **1** and 2.5 mol % of [allylPdCl]<sub>2</sub> were used. <sup>f</sup> Ratio (*E,E*)/(*E,Z*). <sup>g</sup> Ratio (*Z,E*)/(*Z,Z*)+( *E,E*). <sup>h</sup> Ratio (*Z,Z*)/all other isomers.

diene **5** which presumably arose from a cine rearrangement pathway that was also observed previously. Stereospecificity, again, is similar to that obtained with aryl iodides, and some loss in configurational homogeneity of the double bond arising from the silanol is observed, whereas the double bond originating from the iodide is not affected. In entry 5, up to 10% of the stereoisomeric (*E,Z*)-**4** was formed; although this compound may be prone to isomerization, there is almost twice as much isomerization as with silacyclobutane. In this case a different palladium catalyst, [allylPdCl]<sub>2</sub>, had to be used, as Pd(dba)<sub>2</sub> was not effective and led to even more isomerization. When the methyl groups on the starting silanols were replaced with isopropyl groups (entries 2 and 6), the selectivities were again improved to the ratios observed with silacyclobutane.

The dramatic difference between the rate of coupling of the alkenylsilanols in this report and those described recently by Hiyama merits comment. Foremost among probable explanations is the use of different palladium sources and activators. Hiyama employs Pd(PPh<sub>3</sub>)<sub>4</sub> and silver(I) oxide in DMF solution. In our hands, phosphine ligands inhibit the process, but other additives can be helpful to keep the palladium from precipitating in slow coupling reactions.<sup>4b,14</sup> Furthermore, we have found that either tetrabutylammonium fluoride or hydroxide is an effective promoter. Our working hypothesis invokes an important association between the silanol and the palladium center prior to and facilitating the

transmetalation event.<sup>15</sup> Both types of activators (R<sub>4</sub>N<sup>+</sup>X<sup>-</sup> and Ag<sub>2</sub>O) are in principle capable of acting as bases to deprotonate the silanol and thus assist in the association with the palladium intermediate. However, they differ in that both fluoride and hydroxide can also act as nucleophiles and further promote the transmetalation by forming silicate complexes. This is probably not possible with silver(I) oxide.

In summary, we have demonstrated that alkenylsilanols can undergo highly stereospecific, palladium-catalyzed cross-coupling reactions with either aryl or vinyl iodides under extremely mild conditions. The reactions proceed cleanly and in high yields with good functional group compatibility. Current investigations focus on the scope of the silanol-based cross-coupling as well as the mechanism of this unique process.

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**Supporting Information Available:** Procedures for the preparation and full characterization of (*E*)-**1**, (*Z*)-**1**, (*E*)-**2**, and (*Z*)-**2**, spectroscopic data for **3a–3e** and **4a–4c**, and representative procedures for coupling reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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