were measured on micromass 7070H model. ^1H NMR spectra were recorded on a Bruker AM 300 spectrometer at 300 MHz in $CDCl_3$ with tetramethylsilane as internal standard.

The spirolactones (**2a–e**) were prepared by the action of DPDM on oxazolones (**1a–e**) in the presence of TEA/benzene.

***cis*-1,2,2,5-Tetraphenyl-6-oxa-4-azaspiro[2.4]hept-4-en-7-one (2a).** In a typical experiment oxazolone **1a** (2.49 g, 10 mmol) was mixed with DPDM (20 mmol) and TEA (20 mmol) in 20 mL of benzene. The reaction mixture was refluxed for 10 h. When the pink color disappeared on the TLC, the reaction mass was concentrated in vacuo, and the resulting oily mass was passed through a column (silica gel of 200 mesh size using the eluent hexane–benzene, 1:1) to give the spirocyclopropane compound **2a** as a colorless solid (2.9 g): mp 170 °C; yield 70%; mass $[M^+]$ 415; IR ($CHCl_3$) 3000, 1820, 1680, 1520, 1040; NMR ($CDCl_3$) δ 3.85 (1 H, s, H_a), 7.02–7.85 (20 H, m, Ar, H); ^{13}C NMR ($CDCl_3$) 78.939 (spirocarbon) 58.885 (Ph-*C*-Ph), 38.96 (Ph-*C*-H). Anal. Calcd: C, 83.58; H, 5.06; N, 3.37. Found: C, 83.28; H, 5.02; N, 3.42.

Spirocyclopropane lactones **2b–e** were also obtained by the same procedure.

***cis*-1-Benzamido-2,2,3-triphenylcyclopropanecarboxylic Acid (3).** Compound **2a** (2 mmol) was refluxed in 5 mL of 20% NaOH solution in 25 mL of dioxane for 45 min. The resulting reaction mixture was neutralized with 10% HCl, and the compound was extracted with methylene chloride. After the removal of the solvent the compound was obtained as a pure colorless solid (0.68 g, 80% yield): mass $[M^+]$ 433; IR ($CHCl_3$) 3420, 1730, 1660; ^1H NMR ($CDCl_3$) δ 4.87 (1 H, m, H_a), 4.11 (1 H, s, D_2O exchanged), 7.32–7.8 (20 H, m, ArH).

Methyl 1-Benzamido-2,2,3-triphenylcyclopropanecarboxylate (4). Five millimoles of **2a** suspended in 60 mL of absolute methanol and 25 mmol of DMAP was stirred at 70–80 °C for 2 h. The solvent was removed in vacuo, and the residual mass was taken into CH_2Cl_2 and washed with 5% citric acid solution. The organic layer was dried over anhydrous magnesium sulfate and on concentration gave 1.9 g (85%) of crude ester: mass $[M^+]$ 447; IR ($CHCl_3$) 3380, 1720, 1665; ^1H NMR ($CDCl_3$) δ 3.48 (3 H, s, Me*H*), 4.28 (1 H, s, H_a), 7.11–7.86 (20 H, m, Ar*H*).

1-Benzamido-1-(hydroxymethyl)-2,2,3-triphenylcyclopropane (5). To a stirred mixture of LAH (40 mmol) in dry THF (50 mL) was added **2a** (2 mmol) during 30 min under a nitrogen atmosphere. The resultant mixture was stirred for an additional 5 h at 28 °C. At the end of the reaction the contents were treated with ethyl acetate and THF (1:9) and hydrolyzed with 10% aqueous HCl at 0–5 °C. The resulting mass is filtered and extraced with benzene and dried over anhydrous Na_2SO_4. Concentration of the organic layer gave crystalline product (0.756 g; 90% yield) after standing overnight in the refrigerator: mp 182 °C; mass $[M^+]$ 420; IR ($CHCl_3$) 3500, 3000, 1665, 1490, 1040; ^1H NMR ($CDCl_3$) δ 3.28 (1 H, s, H_a), 3.66 (1 H, d, methylene H_b), 4.13 (1 H, d, methylene H_c), 4.09 (1 H, s, hydroxy H). Anal. Calcd: C, 82.93; H, 5.99; N, 3.33. Found: C, 82.61; H, 5.91; N, 3.29.

1-Amino-1-[(benzoyloxy)methyl]-2,2,3-triphenylcyclopropane (6). A solution of **5a** (2 mmol) in dioxane (40 mL) was mixed with 10 N HCl (2 mL), and the mixture was stirred at room temperature for 10–12 h. The solvent was removed under reduced pressure, and the residue was extracted with ether. The ether layer was successively washed with water and 2% aqueous $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. Removal of the solvent gave an oily residue, which on trituration with petroleum ether gave the product as fine crystals, which were stored under nitrogen atmosphere (0.672 g, 80% yield): mp 161 °C; mass $[M^+]$ 420; IR ($CHCl_3$) 3240, 3000, 1720, 1030; ^1H NMR ($CDCl_3$) δ 1.55 (2 H, s, amino H), 3.06 (1 H, s, H_a), 4.29 (1 H, d, H_b), 4.32 (1 H, d, H_c), 6.53–7.21 (20 H, m, ArH). Anal. Calcd: C, 82.93; H, 5.99; N, 3.33. Found: C, 82.03; H, 5.92; N, 3.32.

Acknowledgment. We are thankful to Dr. A. V. Rama Rao, for encouragement. One of us (K.L.) is grateful to CSIR, New Delhi, for the award of Senior Research Fellowship and thankful to Dr. J. M. Rao and Dr. M. Pardhasaradhi for useful discussions, to Mr. Raju for carrying out NOE experiments, and Dr. J. Annapurna for carrying out the activity tests.

Registry No. 1a, 17606-70-1; **1b**, 38879-46-8; **1c**, 15732-43-1; **1d**, 59759-76-1; **1e**, 52956-46-4; **2a**, 118896-81-4; **2b**, 118896-82-5; **2c**, 118896-83-6; **2d**, 118896-84-7; **2e**, 118896-85-8; **3**, 118896-86-9; **4**, 118896-87-0; **5**, 118896-88-1; **6**, 118896-89-2; Ph_2CN_2, 883-40-9.

Stereoselective Palladium-Catalyzed Synthesis of (*Z*)-Trimethyl(2-arylethenyl)silanes by Arylation of (*E*)-1,2-Bis(trimethylsilyl)ethylene. Effects of Added Halides Compared to Silver Salts

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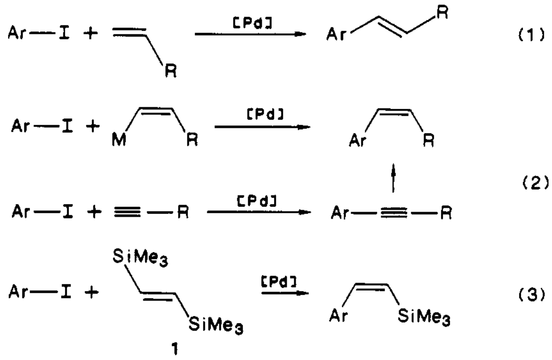
Introduction

Palladium-catalyzed vinylation of aryl halides (the Heck arylation) is of the utmost importance in organic synthesis.[1] Reactions with monosubstituted olefins furnish *E* β-arylated alkenes in high yields (eq 1), and there are to our knowledge no examples of synthetically useful arylations producing the *Z* isomers as the major products.[2] The *Z* isomers can easily be prepared by a stereoselective, palladium-catalyzed cross coupling reaction.[3] When aryl halides (or aryl triflates) are chosen as one of the counterparts,[4] coupling with the proper alkenylmetals[5] or, alternatively, acetylenes[6] followed by hydrogenation, gives the desired products (eq 2).

We here report a Heck-type reaction, which affords fair yields of (*Z*)-trimethyl(2-arylethenyl)silanes from (*E*)-1,2-bis(trimethylsilyl)ethylene (1) and aryl iodides (eq 3), and we have thereby taken advantage of a trimethylsilyl/palladium halide syn-elimination process.



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(1) (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic: London, 1985.

(2) Under certain reaction conditions, highly polarized olefins, such as vinyl ethers, provide predominantly *Z* isomers, and these olefins also tend to result in 1,1-disubstituted products: Andersson, C.-M.; Hallberg, A.; Daves, G. D., Jr. *J. Org. Chem.* **1987**, *52*, 3529.

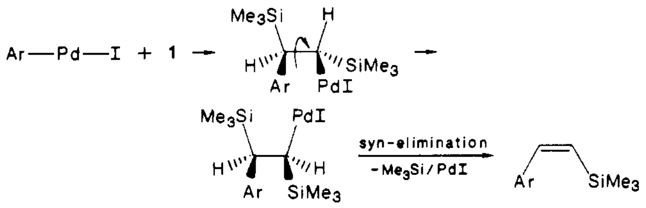
(3) For palladium-catalyzed cross coupling reactions of alkenylmetals with unsaturated halides in general, see for example: (a) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. (b) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393. (c) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749. (d) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (e) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669.

(4) Alternatively, cross coupling of vinyl halides with arylmetals has been used successfully. See for example: (a) Murahashi, S.-I.; Yamamura, M.; Yanagisawa, K.-i.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408. (b) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Komada, S.-i.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.

(5) For palladium-catalyzed preparation of *Z* β-arylated alkenes. (a) From (*Z*)-dialkenyl cuprates and aryl iodides, in the presence of $ZnBr_2$: Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1981**, *22*, 3851. (b) From (*Z*)-alkenyltin reagents and aryl triflates, in the presence of LiCl: Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

(6) (a) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253. (b) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem.* **1975**, *93*, 259. (c) Weir, J. R.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 4926.

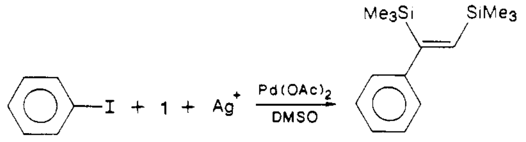
Scheme I



Results and Discussion

Treatment of aryl iodides with (*E*)-1,2-bis(trimethylsilyl)ethylene (**1**) in the presence of triethylamine and a catalytic amount of palladium acetate provides the *Z* olefins in 25–57% isolated yield. The preparative results are summarized in Table I. A GC analysis of the crude product before chromatography revealed that the *Z*/*E* isomers were formed in a ratio of >13, along with <8% of trimethyl(1-arylethenyl)silanes. The corresponding biaryls were the major byproducts, and although easily separated from the reaction mixtures, the biaryl formation limited the yields of **2–6** considerably. The nondesilylated products were present in the reaction mixtures in a yield of <5%.

A possible mechanistic rationale for the formation of **2–6** is given in Scheme I. We believe that the initially formed oxidative addition complex, after olefin insertion, undergoes a syn-elimination process to furnish the (*Z*)-trimethyl(2-arylethenyl)silanes. Thus, we exclude involvement of an anti-elimination[7] and also that the concomitant desilyation observed recently in arylations of trimethylvinylsilane[8,9] is due to Si–C bond cleavage from a Si–C–Pd–I intermediate,[10] since we expected trimethyl(1-arylethenyl)silanes to be formed in the latter case. The presence of halide in the reaction intermediates seems essential for promoting desilylation, and the addition of silver ions as halide abstractors has recently been found, with trimethylvinylsilane as the substrate, to suppress the desilylation and enhance the rate of the reaction.[9] Analogously, (*Z*)-1,2-bis(trimethylsilyl)phenylethylene (**7**) was isolated in 40% yield (65% GC) after reaction of iodobenzene with **1** in the presence of silver nitrate (eq 4). However, a considerable amount, 15% (29% GC), of **2** resulting from desilylation was also observed.



(4)

7

The actual role of the halide in the desilylation process is still obscure. We have considered two alternative explanations for a syn-elimination process: first an elimination of trimethylsilyl iodide and palladium(0) via a five-membered cyclic intermediate,[11] and secondly an elimination of trimethylsilyl palladium iodide, possibly via a Pd–Si interaction in a four-membered transition state.[12] We anticipated that the nature of the halide ion should be more crucial in the first case, and to test this hypothesis we wished to have access to various organopalladium halides for a comparison of the [SiMe$_3$, PdX]/[HPdX] elimination ratio.

Stille has reported that aryl triflates (trifluoromethane sulfonates) are useful in palladium-catalyzed coupling reactions, provided that lithium chloride is added.[5b] It was suggested that the chloride is necessary in order to produce arylpalladium chloride. This approach, to form organopalladium halides in situ, was appealing, since in principle it enables a comparison of various arylpalladium halides in this study.[13] In a control experiment, 4-nitrophenyl triflate was treated with **1** in the presence of lithium iodide. The same product distribution as with the corresponding 1-iodo-4-nitrobenzene was obtained. A very small amount of the nondesilylated product was formed. No significant alteration of the [SiMe$_3$, PdX]/[HPdX] elimination ratio was observed by the addition of LiBr or LiCl.[14] Although speculative, we therefore suggest that a four-membered intermediate is more likely to be involved.

Our next objective was to evaluate the role of halide in the arylation of trimethylvinylsilane. In this case a [HPdX] elimination–readdition probably precedes the desilylation. Reaction of trimethyl(1-deuterioethenyl)silane with 4-nitrophenyl triflate or with 1-iodo-4-nitrobenzene in the presence of silver nitrate yielded (*E*)-trimethyl[2-(4-nitrophenyl)ethenyl-*1-d*]silane. Neither desilylation nor scrambling of the deuterium atom took place. The aryl triflate reaction is considerably slower, which is substantiated by the fact that only traces of product were obtained with phenyl triflate as substrate.

The addition of 3 equiv of LiI to the reaction of 4-nitrophenyl triflate (110 °C, 2 h) enhanced the reaction rate and provided a similar ratio of desilylated/nondesilylated products (4/1) and a similar isomer distribution of deuterated 4-nitrostyrenes as in reaction with 1-iodo-4-nitrobenzene. A comparison of the outcome after the addition of LiI, LiBr, or LiCl revealed that all of the halides promoted desilylation and the ratio was >3/1 in all cases. Addition of LiF resulted in a very slow conversion, and no sign of promotion of desilylation was observed. The addition of LiCl tended to give the most desilylation (7/1). The interpretation of these results is not unequivocal but most likely reflects tendencies of various [HPdX] toward readdition or elimination from the intermediate [HPdX] π-olefin complex.

Conclusion

In conclusion, we think that the synthesis of (*Z*)-trimethyl(2-arylethenyl)silanes from aryl iodides described here is a useful complement to other existing methods for the preparation of this type of compounds.[15] The method merits attention due to the simplicity of the experimental procedure and the expected tolerance to a wide range of substituents in the aryl group.[1] We anticipate that the desilylation discussed, proceeding via a stereoselective

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(7) An example of anti-elimination of stannylpalladium species in palladium-catalyzed reactions of α-styrylstannanes with arenediazonium salts to produce (*Z*)-stilbenes has appeared: Kikukawa, K.; Umekawa, H.; Matsuda, T. *J. Organomet. Chem.* **1986**, *311*, C44.

(8) Hallberg, A.; Westerlund, C. *Chem. Lett.* **1982**, 1993.

(9) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286.

(10) For a review on the cleavage of C–Si bonds by palladium compounds, see: Akhrem, I. S.; Chistovalova, N. M.; Vol'pin, M. E. *Russ. Chem. Rev.* **1983**, *52*, 542.

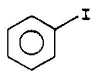
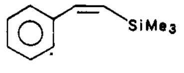
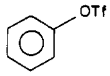
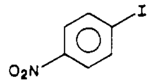
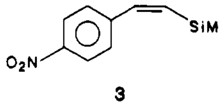
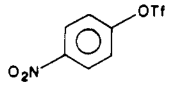
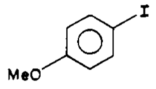
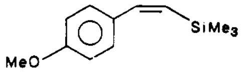
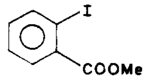
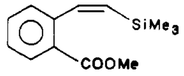
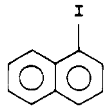
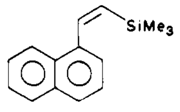
(11) The desilylation involved in the formation of 3-(polyfluoroalkyl)-1-propenes through the Fe$_3$(CO)$_{12}$- or Ru$_3$(CO)$_{12}$-catalyzed reaction of polyfluoroalkyl halides with allylsilanes has been suggested to occur via similar intermediates: Fuchikami, T.; Ojima, I. *Tetrahedron Lett.* **1984**, *25*, 307.

(12) (a) For a discussion of Pd–Si interaction in C–Si bond cleavage, see: Akhrem, I. S.; Chistovalova, N. M.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser Khim.* **1983**, 2696. (b) An example of a stable compound with a coordinative Pd–Si bond has been described: Grobe, J.; Martin, R.; Möller, U. *Angew. Chem.* **1977**, *89*, 257.

(13) Aryl chlorides do not undergo oxidative addition under the reaction conditions, catalytic in palladium. For exceptions in related systems, see: (a) Julia, M.; Duteil, M. *Bull. Soc. Chim. Fr.* **1973**, 2790. (b) Julia, M.; Duteil, M.; Grard, C.; Kuntz, E. *Bull. Soc. Chim. Fr.* **1973**, 2791. (c) Davison, J. B.; Simon, N. M.; Sojka, S. A. *J. Mol. Catal.* **1984**, *22*, 349. (d) For a related work on nickel(0) and aryl chlorides see: Bozell, J. J.; Vogt, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 2655.

(14) No conversion of 4-nitrophenyl triflate was observed after addition of LiF under similar reaction conditions.

Table I. Palladium-Catalyzed Arylation of (*E*)-1,2-Bis(trimethylsilyl)ethylene[a]

entry	starting material	isolated yield, %	product
1		43	 **2**
2	 + 3LiI	trace	**2**
3		23[b]	 **3**
4	 + 3LiI	25[b]	**3**
5		57	 **4**
6		49	 **5**
7		55	 **6**

[a] The reactions were carried out in the presence of triethylamine, in DMF (110 °C, 2 h) with palladium acetate as catalyst precursor. [b] About 40% yield of 4,4′-dinitrobiphenyl was also isolated.

[$SiMe_3$, PdI] syn-elimination process, could possibly also be utilized for the preparation of other (*Z*)-1,2-disubstituted olefins by employing (*E*)-2-substituted vinylsilanes.

Experimental Section

Materials. Aryl Iodides. Iodobenzene (Fluka), 1-iodo-4-nitrobenzene (Janssen), 1-iodo-4-methoxybenzene (Fluka), and 1-iodonaphthalene (Aldrich) were used as received from the commercial sources indicated. 2-Iodobenzoic acid methyl ester was generously supplied by Dr. L.-G. Wistrand.

Aryl Triflates. Phenyl triflate and 4-nitrophenyl triflate were prepared according to a literature method.[16]

Vinylic Silanes. (*E*)-1,2-Bis(trimethylsilyl)ethylene[17] was prepared by treatment of (*E*)-trimethyl(2-bromoethenyl)silane (Fluka) with *t*-BuLi (2.1 equiv) in THF and subsequent quenching with chlorotrimethylsilane. Trimethyl(1-deuterioethenyl)silane[18] was prepared by treatment of 18 mmol of trimethyl(1-bromoethenyl)silane (Fluka) with *t*-BuLi (2.1 equiv) in THF, and the generated anion was quenched with deuterated water. The resulting solution was diluted with pentane, washed several times with water, and dried with $MgSO_4$. The concentration of the trimethyl(1-deuterioethenyl)silane in the pentane solution was estimated to be 0.2 M. Portions of 15 mL of the pentane solution were used for the deuterated experiments.

Other Reagents. Palladium acetate (Fluka), silver nitrate (Merck), triethylamine (Merck), dimethyl formamide (Janssen), dimethyl sulfoxide (Janssen), and the lithium salts (Merck) were used as received from the commercial sources indicated.

General Procedures. The NMR spectra were recorded on a Varian XL 300 (300 MHz, ^{1}H; 46 MHz, ^{2}H). The ^{1}H NMR shifts are given relative to TMS in deuteriochloroform, and ^{2}H NMR shifts are given relative to TMS-d_{12} in chloroform. Mass spectra were obtained on a Finnigan 4021 (Data System Incos 2100) gas chromatography/mass spectrometer at 70 eV. Deuterium contents were estimated by mass spectroscopy at 16 or 70 eV. Gas chromatographic analyses were performed on a Varian 3300 instrument equipped with a (2.5 m × 2 mm) glass column of 5% OV 17 on Chromosorb W. Elemental analyses were performed by Dornis u. Kolbe Microanalytical Laboratory, Mülheim, West Germany. Column chromatography was carried out using E. Merck silica gel 60 (0.040–0.063 mm) and pentane or pentane/ether (17:1) as eluent. All reactions were run in a 100-mL heavy-walled, thin-necked Pyrex tube, sealed with a Teflon stopcock, and with magnetic stirring.

General Procedure for the Arylation of (*E*)-1,2-Bis(trimethylsilyl)ethylene. Each of the reactants was dissolved or dispersed in dimethylformamide (a total of 2 mL) and was added to a Pyrex tube: palladium acetate (16.8 mg, 0.075 mmol), aryl iodide (2.5 mmol) or aryl triflate (2.5 mmol)/lithium halide (7.5 mmol), (*E*)-1,2-bis(trimethylsilyl)ethylene (1) (860 mg, 5.0 mmol), and triethylamine (606 mg, 6.0 mmol). A considerably slower reaction was achieved with 2.5 mmol of 1. The contents were

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(15) Selected methods for preparation of (*Z*)-trimethyl(2-arylethenyl)silanes were from the following references. From trimethyl(phenylethynyl)silane and reducing agents: (a) Benkeser, R. A.; Hickner, R. A. *J. Am. Chem. Soc.* **1958**, *80*, 5298. (b) Seyferth, D.; Vaughan, L. G.; Suzuki, R. *J. Organomet. Chem.* **1964**, *1*, 437. (c) Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520. (d) Miller, B. R.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424. (e) Sato, F.; Ishikawa, H.; Sato, M. *Tetrahedron Lett.* **1981**, *22*, 85. From (*Z*)-2-styryllithium derivatives and trimethylsilyl chloride: (f) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017. From (*Z*)-4-phenyl-3-(trimethylsilyl)-2-oxetanone by decarboxylation: (g) Zaitseva, G. S.; Vinokurova, N. G.; Baukov, Yu, I. *Zh. Obshch. Khim.* **1975**, *45*, 1398. The following synthetic methods gives *E*/*Z* mixtures of trimethyl(2-arylethenyl)silanes. From alkanesulfonyl chlorides and (trimethylsilyl)diazomethane: (h) Aoyama, T.; Toyama, S; Tamaki, N.; Shioiri, T. *Chem. Pharm. Bull.* **1983**, *31*, 2957. From α-silyl carbanions and aryl aldehydes: (i) Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852. (j) Ager, D. J. *J. Org. Chem.* **1984**, *49*, 168. From styrylhalides by electrochemical silylation: (k) Yoshida, J.-i.; Muraki, K.; Funahashi, H.; Kawabata, N. *J. Org. Chem.* **1986**, *51*, 3996.

(16) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

(17) (a) Bock, H.; Seidl, H. *J. Organomet. Chem.* **1968**, *13*, 87. (b) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1978**, *144*, 1.

(18) Soderquist, J. A.; Hassner, A. *J. Organomet. Chem.* **1981**, *217*, 151.

(19) (a) Dohner, B. R.; Saunders, W. H., Jr. *Can. J. Chem.* **1986**, *64*, 1026. (b) Choi, H-S; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 901.

heated and magnetically stirred at 110 °C for 2 h and thereupon poured into 10 mL of water. After extraction with pentane (4 × 10 mL), the combined organic phases were washed with 5 mL of water, dried ($MgSO_4$), and evaporated. The crude product was subjected to column chromatography.

Reaction of 1-Iodo-4-nitrobenzene or 4-Nitrophenyl Triflate/Lithium Iodide with Trimethyl(1-deuterioethenyl)silane. A mixture of palladium acetate (0.03 mmol, 6.7 mg), 1-iodo-4-nitrobenzene (1.0 mmol, 249 mg) or 4-nitrophenyl triflate (1.0 mmol, 271 mg)/lithium iodide (3.0 mmol, 402 mg), triethylamine (3.0 mmol, 303 mg), dimethylformamide (5 mL), and 15 mL of the pentane solution containing about 3 mmol of trimethyl(1-deuterioethenyl)silane (see above) were added to a Pyrex tube and stirred vigorously at 110 °C for 2 h. After workup as above, column chromatography (pentane/ether, 17:1) yielded about 25% of the deuterated styrene derivatives (>95% D). The ^{1}H NMR shifts were in accordance with those previously reported.[19] The ^{2}H NMR spectrum showed three singlets at 5.56, 5.99, and 6.84 ppm corresponding to (*Z*)-1-(ethenyl-*2-d*)-4-nitrobenzene, (*E*)-1-(ethenyl-*2-d*)-4-nitrobenzene, and 1-(ethenyl-*1-d*)-4-nitrobenzene respectively. Integration of the signals gave the proportions of 25/70/5 from 1-iodo-4-nitrobenzene and 38/55/7 from 4-nitrophenyl triflate/lithium iodide.

Reaction of 1-Iodo-4-nitrobenzene/Silver Nitrate or 4-Nitrophenyl Triflate with Trimethyl(1-deuterioethenyl)silane. A mixture of palladium acetate (0.03 mmol, 6.7 mg), 1-iodo-4-nitrobenzene (1.0 mmol, 249 mg)/silver nitrate (2.0 mmol, 340 mg) or 4-nitrophenyl triflate (1.0 mmol, 271 mg), triethylamine (3.0 mmol, 303 mg), dimethyl sulfoxide (10 mL), and 15 mL of the pentane solution containing about 3 mmol of trimethyl(1-deuterioethenyl)silane (see above) were added to a Pyrex tube, stirred, and heated for 5 and 6 h, respectively. For the triflate reaction, additional catalyst (2 mol %) was added after 2 and 4 h. After workup as above, column chromatography gave 35–40% yield of (*E*)-trimethyl[2-(4-nitrophenyl)ethenyl-*1-d*]silane. ^{2}H NMR showed a singlet peak at 6.80 ppm (>98% D). Structural assignment was based on comparison with the chemical shifts in the corresponding ^{1}H NMR spectrum.[9]

Arylation of (*E*)-1,2-Bis(trimethylsilyl)ethylene with Iodobenzene in the Presence of Silver Nitrate. Each of the reactants was dissolved or dispersed in dimethyl sulfoxide (a total of 15 mL) and was added to a Pyrex tube in the following order: palladium acetate (0.03 mmol, 6.7 mg), silver nitrate (1.5 mmol, 255 mg), iodobenzene (1.5 mmol, 306 mg), triethylamine (3.0 mmol, 303 mg), and (*E*)-1,2-bis(trimethylsilyl)ethylene (2.7 mmol, 470 mg). The contents were heated and stirred at 70 °C for 6 h. Additional catalyst (0.03 mmol, 6.7 mg) was added after 2 and 4 h. After workup as above, the crude mixture was filtered through a short column of silica gel. Separation by HPLC (CH_3CN, 500 mm RP Polygosil C_{18} (5 μm) column) gave 40 mg (15%) of **2** and 150 mg (40%) of **7** (*Z*/*E* = 95:5). The ^{1}H NMR spectrum of **7** matched the literature spectrum.[20]

(*Z*)-Trimethyl(2-phenylethenyl)silane (2). Chromatography gave 43% of **2**, with an isomeric purity of >94%. The contaminating isomers were trimethyl(1-phenylethenyl)silane (3%) and (*E*)-trimethyl(2-phenylethenyl)silane (2%). The ^{1}H NMR spectrum matched that previously reported.[15b]

(*Z*)-Trimethyl[2-(4-nitrophenyl)ethenyl]silane (3). Chromatography gave 23–25% of **3**, with an isomeric purity of 95%. The contaminating isomers were trimethyl[1-(4-nitrophenyl)ethenyl]silane (4%) and (*E*)-trimethyl[2-(4-nitrophenyl)ethenyl]silane (1%). The ^{1}H NMR spectrum matched that previously reported.[15h] About 40% yield of 4,4′-dinitrobiphenyl was also isolated.

(*Z*)-Trimethyl[2-(4-methoxyphenyl)ethenyl]silane (4). Chromatography gave 57% of **4**, with an isomeric purity of 95%. The contaminating isomers were trimethyl[1-(4-methoxyphenyl)ethenyl]silane (3%) and (*E*)-trimethyl[2-(4-methoxyphenyl)ethenyl]silane (2%): ^{1}H NMR δ 0.08 (s, 9 H), 3.82 (s, 3 H), 5.72 (d, J = 15.1 Hz, 1 H), 6.84–7.25 (m, 4 H), 7.30 (d, J = 15.0 Hz, 1 H); MS *m/e* (rel intensity) 206 (M^+, 40), 191 (100), 175 (45), 165 (50), 161 (10), 145 (7), 131 (7), 115 (7), 96 (7), 89 (10), 73 (8), 59 (60), 45 (25). Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.8; H, 8.79. Found: C, 69.4; H, 8.57.

(*Z*)-Trimethyl[2-(2-carbomethoxyphenyl)ethenyl]silane (5). Chromatography gave 49% of **5**, with an isomeric purity of 96%. The contaminating isomers were trimethyl[1-(2-carbomethoxyphenyl)ethenyl]silane (2%) and (*E*)-trimethyl[2-(2-carbomethoxyphenyl)ethenyl]silane (2%): ^{1}H NMR δ –0.11 (s, 9 H), 3.88 (s, 3 H), 5.88 (d, J = 15.1 Hz, 1 H), 7.76 (d, J = 15.1 Hz, 1 H), 7.26–7.96 (m, 4 H); MS *m/e* (rel. intensity) 234 (M^+, 5), 219 (10), 203 (5), 187 (5), 173 (5), 161 (70), 145 (40), 130 (10), 115 (10), 102 (10), 89 (100), 73 (35), 59 (60), 45 (25). Anal. Calcd for $C_{13}H_{18}O_2Si$: C, 66.6; H, 7.74. Found: C, 66.9; H, 7.51.

(*Z*)-Trimethyl(2-naphth-1-ylethenyl)silane (6). Chromatography gave 55% of **6**, with an isomeric purity of 95%. The contaminating isomers were trimethyl(1-naphth-1-ylethenyl)silane (3%) and (*E*)-trimethyl(2-naphth-1-ylethenyl)silane (2%): ^{1}H NMR δ –0.13 (s, 9 H), 6.11 (d, J = 15.4 Hz, 1 H), 7.82 (d, J = 15.4 Hz, 1 H), 7.32–8.00 (m, 7 H); MS *m/e* (rel intensity) 226 (M^+, 10), 211 (10), 195 (10), 183 (9), 167 (10), 165 (10), 152 (45), 73 (80), 59 (100), 45 (15). Anal. Calcd for $C_{15}H_{18}Si$: C, 79.6; H, 8.01. Found: C, 79.6; H, 7.98.

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Registry No. 1, 18178-59-1; (*Z*)-**2**, 19319-11-0; (*E*)-**2**, 19372-00-0; (*Z*)-**3**, 88691-48-9; (*E*)-**3**, 85260-63-5; (*Z*)-**4**, 119327-32-1; (*E*)-**4**, 76711-42-7; (*Z*)-**5**, 119327-33-2; (*E*)-**5**, 101047-41-0; (*Z*)-**6**, 119327-34-3; (*E*)-**6**, 105281-55-8; (*Z*)-**7**, 53511-11-8; (*E*)-**7**, 53511-10-7; LiI, 10377-51-2; Pd(OAc)$_2$, 3375-31-3; iodobenzene, 591-50-4; 1-iodo-4-nitrobenzene, 636-98-6; 1-iodo-4-methoxybenzene, 696-62-8; 1-iodonaphthalene, 90-14-2; 2-iodobenzoic acid methyl ester, 610-97-9; phenyl triflate, 17763-67-6; 4-nitrophenyl triflate, 17763-80-3; trimethyl(1-deuterioethenyl)silane, 79678-00-5; (*Z*)-1-(ethenyl-*2-d*)-4-nitrobenzene, 89039-14-5; (*E*)-1-(ethenyl-*2-d*)-4-nitrobenzene, 104960-13-6; 1-(ethenyl-*1-d*)-4-nitrobenzene, 57204-41-8; silver nitrate, 7761-88-8; (*E*)-trimethyl[2-(4-nitrophenyl)ethenyl-*1-d*]silane, 119327-36-5; trimethyl(1-phenylethenyl)silane, 1923-01-9; trimethyl[1-(4-nitrophenyl)ethenyl]silane, 94397-83-8; trimethyl[1-(4-methoxyphenyl)ethenyl]silane, 107099-29-6; trimethyl[1-(2-carbomethoxyphenyl)ethenyl]silane, 119327-37-6; trimethyl(1-naphth-1-ylethenyl)silane, 119327-35-4; 4,4′-dinitrobiphenyl, 1528-74-1.

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(20) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51.