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Synthesis of 1-Trimethylsilyl 1,3-Dienes by the Palladium-Catalyzed Reaction of Trimethylvinylsilane with Vinyl Iodides/Silver Nitrate or Vinyl Triflates

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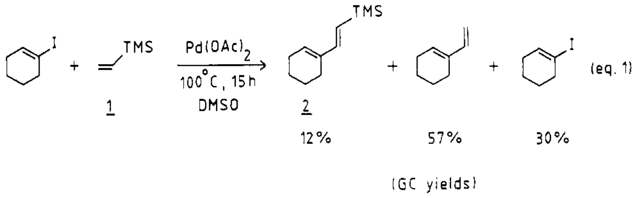
A series of 1-trimethylsilyl 1,3-dienes has been synthesized by a palladium-catalyzed coupling of trimethylvinylsilane (1) either with vinyl halides in the presence of silver salts or alternatively with vinyl triflates. Apart from enhancing the rate of the reaction considerably, silver nitrate suppresses the desilylation. For example, while (*E*)-trimethyl[2-(cyclohex-1-en-1-yl)ethenyl]silane (2) is obtained in fair yield from 1 and 1-cyclohexenyl iodide/silver nitrate or 1-cyclohexenyl triflate, 1-ethenylcyclohexene is the dominant product under ordinary Heck reaction conditions, catalytic in palladium.

Introduction

Multifunctionalized 1-trimethylsilyl 1,3-dienes often exhibit high reactivity and regio- and stereospecificity toward dienophiles[1] and electrophiles.[2] Consequently, these dienes are becoming well established as useful intermediates in organic synthesis, suggesting that efficient synthetic methods[3] for their preparation are desirable. Palladium-catalyzed vinylation of olefins, the Heck reaction,[4] should in principle serve as an attractive alternative preparative route to some of these important dienes, provided a high regioselectivity[5] can be achieved, and the concomitant desilylation[6] reaction can be suppressed. Here we report that palladium-catalyzed vinylation of trimethylvinylsilane (1), either with vinyl halides in the presence of silver salts[7,8] or with vinyl triflates[9] (trifluoromethanesulfonates), furnishes 1-trimethylsilyl 1,3-dienes, a class of compounds recognized to result in valuable allylsilanes after reaction with olefins.[1]

Results

Vinyl Iodides. Application of the commonly used Heck reaction conditions[10] to the reaction of 1-cyclohexenyl iodide with trimethylvinylsilane (1) in DMSO resulted in desilylation, and only 12% (GC) of the desired nondesilylated diene 2 was formed. A considerable amount of the starting material, 30%, remained after 16 h at 100 °C (eq 1).



However, our recent discovery that the desilylation occurring in the palladium-catalyzed arylation of vinylsilanes[8] and allylsilanes[11] can be suppressed by the addition of silver ions prompted us to apply the same methodology in this study.

The addition of silver nitrate has now been found to exert the same effect in the vinylation reactions,[12] allowing

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(1) (a) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415. (b) Jung, M. E.; Gaede, B. *Tetrahedron* **1979**, *35*, 621. (c) Koreeda, M.; Ciufolini, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 2308. (d) Oppolzer, W.; Burford, S. C.; Marazza, F. *Helv. Chim. Acta* **1980**, *63*, 555. (e) Burke, S. D.; Smith Strickland, S. M.; Powner, T. H. *J. Org. Chem.* **1983**, *48*, 454. (f) For a review on the Diels–Alder reactions of heterosubstituted 1,3-dienes, see: Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753.

(2) (a) Pillot, J.-P.; Dunoguès, J.; Calas, R. *J. Chem. Res., Synop.* **1977**, 268. (b) Yamamoto, K.; Ohta, M.; Tsuji, J. *Chem. Lett.* **1979**, 713. (c) Sleta, T. M.; Stadnichuk, M. D.; Petrov, A. A. *Zh. Obshch. Khim.* **1968**, *38*, 374.

(3) Selected methods for the preparation of 1-trimethylsilyl 1,3-dienes were as follows. From 1-(trimethylsilyl)propynol: (a) See ref 1a and 1b. By addition of silicon hydrides to C–C multiple bonds: (b) Petrov, A. D.; Sadykh-Zade, S. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1958**, 513. (c) Stadnichuk, M. D.; Petrov, A. A. *Zh. Obshch. Khim.* **1963**, *33*, 3563. From 1-(trimethylsilyl)but-3-en-2-ol by dehydration: (d) Sadykh-Zade, S. I.; Petrov, A. D. *Zh. Obshch. Khim.* **1958**, *28*, 1542. (e) See ref 2a. From reactions of carbonyl compounds with the allyltrimethylsilane anion: (f) See ref 1c and 2b. From reactions of carbonyl compounds with the 1,3-bis(trimethylsilyl)propenyl anion: (g) Chan, T.-H.; Li, J.-S. *J. Chem. Soc., Chem. Commun.* **1982**, 969. (h) Corriu, R.; Escudie, N.; Guerin, C. *J. Organomet. Chem.* **1984**, *264*, 207. From silylated sulfones: (i) Bloch, R.; Abecassis, J. *Tetrahedron Lett.* **1983**, *24*, 1247. (j) Chou, T.-S.; Tso, H.-H.; Tao, Y.-T.; Ching Lin, L. *J. Org. Chem.* **1987**, *52*, 244. From hydroalumination of 1-trimethylsilyl 1,3-diynes: (k) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1983**, *105*, 1383. (l) Zweifel, G.; Leong, W. *J. Am. Chem. Soc.* **1987**, *109*, 6409. From palladium-catalyzed coupling of vinyl triflates or vinyl iodides with vinyltin reagents: (m) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (n) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813. From trimethyl(2-bromovinyl)silane with vinylcuprates: (o) Koshutin, V. I.; Nazarenko, N. P. *Zh. Obshch. Khim.* **1982**, *52*, 2376. From 3-(trimethylsilyl)-3-sulfolenes by thermal extrusion of SO_2: (p) Tao, Y.-T.; Chen, M.-L. *J. Org. Chem.* **1988**, *53*, 69.

(4) (a) Heck, R. F. *Org. React. (N.Y.)* **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.

(5) Vinylation of 1-hexene provides regioisomers: Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3898.

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

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(8) For palladium-catalyzed arylation of trimethylvinylsilane in the presence of silver nitrate: (a) Karabelas, K.; Hallberg, A. *Tetrahedron Lett.* **1985**, *26*, 3131. (b) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286.

(9) For palladium-catalyzed coupling of vinyl triflates with olefins: (a) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 2271. (b) Scott, W. J.; Pena, M. R.; Swärd, K.; Stoessel, S. J.; Stille, J. K. *J. Org. Chem.* **1985**, *50*, 2302. (c) Harnisch, W.; Morera, E.; Ortar, G. *J. Org. Chem.* **1985**, *50*, 1990. (d) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1987**, *28*, 3039. (e) Hirota, K.; Kitade, Y.; Isobe, Y.; Maki, Y. *Heterocycles* **1987**, *26*, 355. (f) Pena, M. R.; Stille, J. K. *Tetrahedron Lett.* **1987**, *28*, 6573. For palladium-catalyzed coupling with organostannanes: (g) See ref 3m. (h) Scott, W. J.; Grips, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (i) Stille, J. K.; Tanaka, M. *J. Am. Chem. Soc.* **1987**, *109*, 3785. For carbonylative coupling with organostannanes: (j) Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500. For palladium-catalyzed coupling with organozinc compounds: (k) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Tetrahedron Lett.* **1986**, *27*, 955. (l) Orsini, F.; Pelizzoni, F. *Synth. Commun.* **1987**, *17*, 1389. (m) McCague, R. *Tetrahedron Lett.* **1987**, *28*, 701. (n) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1157.

(10) Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.

(11) Karabelas, K.; Westerlund, C.; Hallberg, A. *J. Org. Chem.* **1985**, *50*, 3896.

(12) Neither silver tetrafluoroborate nor silver triflate showed any advantages over silver nitrate.

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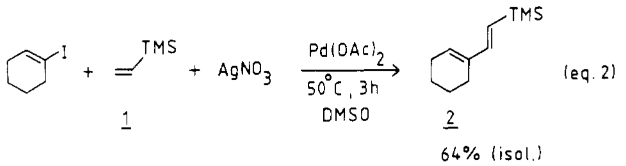
2 to be isolated in 64% yield after 3 h at 50 °C (eq 2). The reaction rate was also substantially enhanced,[13] which is reflected in the fact that only 5% of the vinyl iodide was converted to the desilylated diene under similar reaction conditions in the absence of silver ions.



The reactions of **1** with a series of vinyl iodides and vinyl bromides in the presence of silver nitrate are summarized in Table I. In contrast to 1-cyclohexenyl iodide (entry 1), 1-cyclopentenyl iodide, in addition to **3**, afforded the triene **4** in 25% yield (GC) with DMSO as solvent (entry 3). Excess **1** did not suppress the formation of **4**, suggesting that the diene **3** is at least as reactive as **1**. However, **3** was not observed after reaction in acetonitrile, although a longer reaction time and more catalyst was required to achieve full conversion of the starting material in this solvent (entry 2). Furthermore, of the vinyl halides tested (vide infra), cyclopentenyl iodide is the only halide that is prone to undergo desilylation even in the presence of silver ions: 20% (GC) of the corresponding diene is formed. Reaction of (1-iodovinyl)trimethylsilane with **1** in DMSO furnished, in addition to the diene **5**, the cyclohexadiene **6** (35%, GC), isolated by HPLC. Under workup, **6** is slowly oxidized to 1,3,5-tris(trimethylsilyl)benzene (**7**) (entry 5). No improvement of the yield of **5** was achieved with an excess of **1**. However, in acetonitrile a higher yield of **5** was obtained, provided an additional amount of both **1** and the catalyst was employed, and the formation of **6** was now completely suppressed (entry 4).

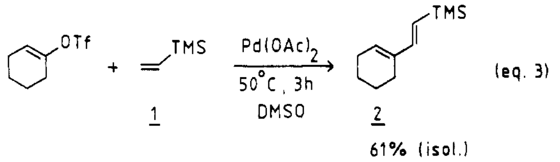
Activation of the vinyl iodide by an electron-withdrawing group, as exemplified in entry 6, resulted in a fast reaction, and (*E*)-trimethyl[2-(1-oxocyclohex-2-en-3-yl)ethenyl]silane (**8**) was isolated in 77% yield. Two double-bond isomers, **9** and **10**, were obtained after reaction of 2-iodohexene with **1**, with the exomethylene diene **9** as the major product (entry 7). The addition of triphenylphosphine or the use of acetonitrile as solvent did not affect the product distribution. The formation of **10** was somewhat unexpected considering the findings by Overman's group that double-bond isomerization is considerably suppressed in the presence of silver ions in their systems.[14]

The importance of the substitution pattern in the vinyl halides for the regiochemical outcome is apparent from comparison of entries 1–7 with entries 8 and 10. Mixtures of regioisomers were obtained both with 1-iodohexene, to give **11** and **12**, and with β-iodostyrene,[15] to give **13** and **14** (entries 8 and 10). The regioselectivity was not affected by employing organopalladium acetates, prepared from the corresponding styrylboronic acid or 1-hexenylboronic acid and a stoichiometric amount of palladium acetate.[10] No desilylation was observed (entries 9 and 11). No improvement of the regioselectivity and low conversion were observed under the phase-transfer conditions reported by Jeffery.[16] Thus, a substituent on the carbon bearing the iodo atom seems essential for achieving a regiocontrolled synthesis. Similar observations were reported by Heck for vinylations of 1-hexene.[5]

Vinyl Bromides. Efforts were made to use the more economical and more easily available vinyl bromides as starting materials. With vinyl bromides, such as 2-bromopropene, (2-bromovinyl)trimethylsilane, (*Z*)-1-bromo-2-ethoxyethylene, and β-bromostyrene, we were unable to obtain more than very low yields of products under a variety of conditions. Thus, in spite of high temperature, i.e., 120 °C, β-bromostyrene resulted in very slow conversion, and a desilylated aryl diene was formed as the major product according to a GC/MS analysis. We have previously experienced that the palladium-catalyzed reaction of bromobenzene with **1** in the presence of silver nitrate is very slow. That is now also found to be the case for vinyl bromides. However, activation of the system by a carbonyl group on the β-carbon of the halide led to a good conversion (entries 12 and 13).

Employing (*E*)-methyl 3-bromopropenoate furnished a mixture of isomers, **15** and **16**, separable by HPLC (entry 12). In attempts to direct the addition of the vinylpalladium species, a series of reactions was performed with phosphine ligands.[17] No significant alteration of the isomer distribution was observed. 3-Bromo-2-cyclohexen-1-one furnished one isomer, as was the case with the corresponding iodide (entry 13). Surprisingly, methyl 2-bromopropenoate did not react despite higher reaction temperature.

Vinyl Triflates. Vinyl triflates have been shown to serve as useful precursors to organopalladium intermediates.[9] Stille has successfully synthesized 1-trimethylsilyl 1,3-dienes by palladium-catalyzed cross coupling of vinyl triflates with (*E*)-1-(trimethylsilyl)-2-(trimethylstannyl)ethylene.[3m] We assumed that a similar product distribution would be obtained in the Heck reactions from vinyl triflates as from vinyl halides/silver salts, because no halides promoting C–Si bond cleavage are present in the former case. In the first experiments we treated cyclohexenyl triflate (eq 3) and cyclopentenyl triflate with **1** in the presence of palladium catalyst and triethylamine (Table II, entries 14 and 15). These vinyl triflates were as reactive as the corresponding vinyl iodides in the presence of silver nitrate, and desilylation was only observed with cyclopentenyl triflate. No triene **4** was formed in DMSO (cf. entry 3). The utility of vinyl triflates as starting materials is further substantiated by the reactions of the bicyclic 6-methoxy-3,4-dihydro-1-naphthalenyl triflate and 1-[(trimethylsilyl)ethynyl]-2,2-dimethylethenyl triflate with **1**. Both furnished good yields of the dienes **17** and **18**, although a considerable amount (13%) of two isomers was found in the first case (entries 16 and 17). Palladium acetate as catalyst precursor is in general considerably more efficient than tetrakis(triphenylphosphine)palladium(0).



Discussion

We assume that palladium catalyzed reactions of vinyl halides in the presence of silver ions and of vinyl triflates proceed via a vinylpalladium intermediate **19**[18,19] (Scheme

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[13] We have observed a similar effect of added silver salts on the reaction rate in the palladium-catalyzed vinylation and arylation of 1-hexene.

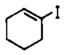
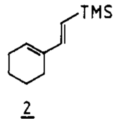
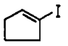
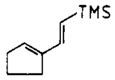
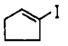
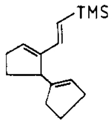
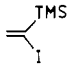
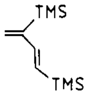
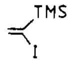
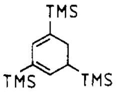
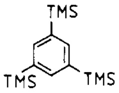
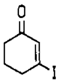
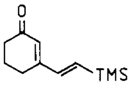
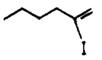
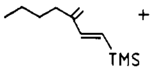
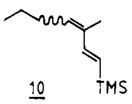
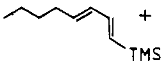
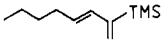
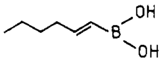
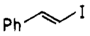
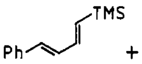
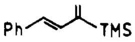
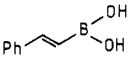
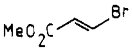
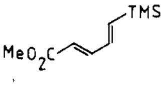
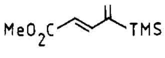
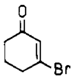
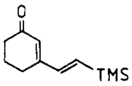
[14] (a) Abelman, M. M.; Oh, T.; Overman, L. E. *J. Org. Chem.* **1987**, *52*, 4130. (b) Abelman, M. M.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 2328.

[15] Vinylation of triethoxyvinylsilane gave a similar regioselectivity.

[16] Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667.

[17] Phosphine ligands screened included PPh_3, $P(o\text{-Tol})_3$, $P(OEt)_3$.

Table I. Palladium-Catalyzed Vinylation of Trimethylvinylsilane with Vinyl Halides in the Presence of Silver Nitrate at 50 °C

entry	starting material	solvent	time,[a] h	isolated[b] yield, %	product(s)
1		DMSO	3	64	 2
2		MeCN	24	36	 3
3		DMSO	3	52[c]	3 +  4
4		MeCN	19	66	 5
5		DMSO	3	55[d]	5 +  6 +  7
6		DMSO	1	77	 8
7		DMSO	3	51	 9 +  10 3.5 : 1
8	[e]	DMSO	2	73	 11 +  12 + others[h] 3 : 1
9		DMSO	2	92[f]	3 : 1
10		DMSO	2	75	 13 +  14 3.5 : 1
11		DMSO	2	95[f]	3.5 : 1
12		DMSO	4[g]	69	 15 +  16 1.5 : 1
13		DMSO	4	70[f]	 8

[a] Unoptimized. [b] An unknown isomer, 3–5%, was present in every case. [c] GC yield of 3. [d] GC yield of 5. [e] The isomeric purity was 96%. [f] GC yield. The reaction was run without $AgNO_3$ but required stoichiometric $Pd(OAc)_2$. [g] Reaction at 20 °C in DMSO gave the same product distribution but required a reaction time of 48 h for complete conversion. [h] Three other isomers, 10%, together with 5% of (*E*,*E*)-5,7-dodecadiene were present according to GC/MS.

Scheme I

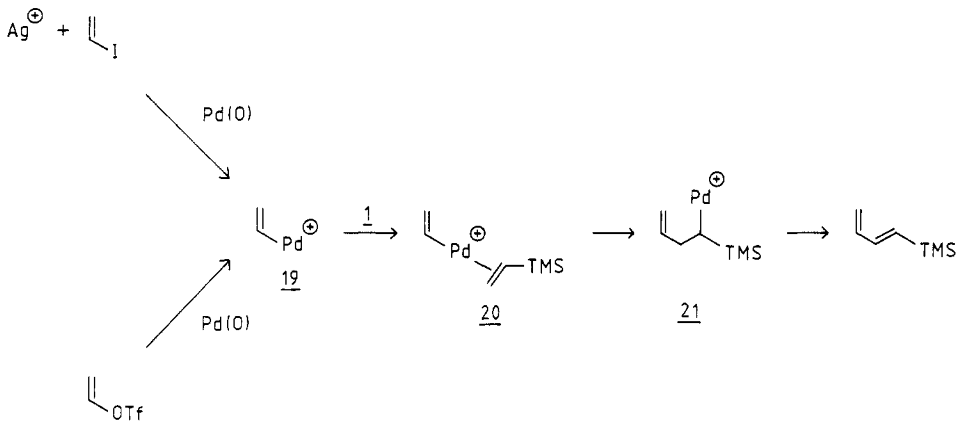
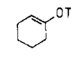
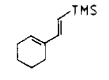
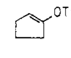
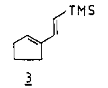
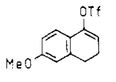
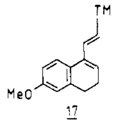
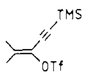
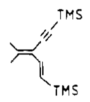
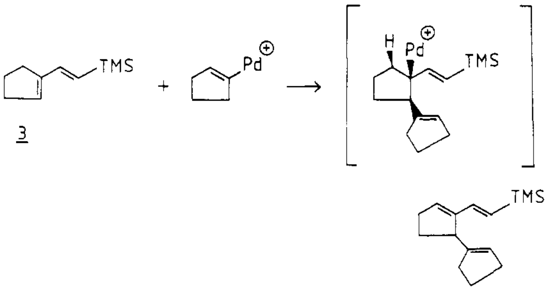


Table II. Palladium-Catalyzed Vinylation of Trimethylvinylsilane with Vinyl Triflates in DMSO

entry	starting material	temp, °C	time, h	isolated[a] yield, %	product(s)
14		50	3	61	 2
15		50	3	38	 3
16		50	3	70	 + others[b] 17 87 13
17		80	1.5	72	 18

[a] An unknown isomer, 3–5%, was present in every case. [b] Two other isomers, 13%, were present according to GC/MS.

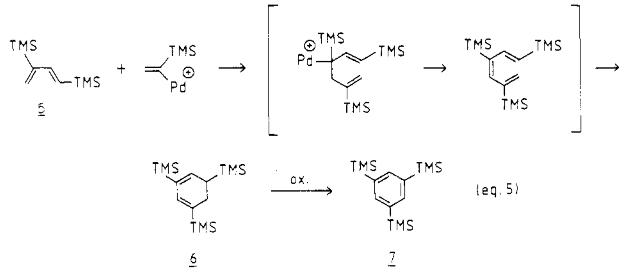
I). This common intermediate forms a tight olefin–palladium complex **20**, and the vinyl group is thereupon transferred, affording the adduct **21**. We believe that the diene is the result of a syn elimination. In support of this is the fact that a cyclopentenylpalladium attack on **3** furnishes the triene **4** and not a conjugated 1,3,5-triene that would require an anti elimination to occur (eq 4).



(eq. 4)

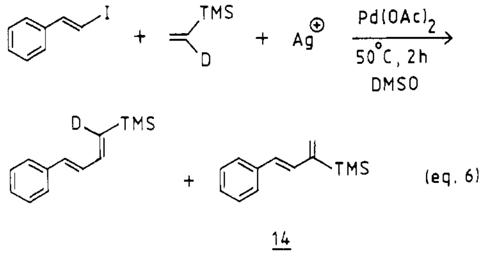
4

In the analogous reaction of **5**, the adduct collapses into the conjugated triene, which results in the cyclohexadiene **6** (eq 5) presumably via an electrocyclic rearrangement.



(eq. 5)

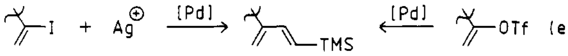
An experiment with β-iodostyrene and (1-deuteriovinyl)trimethylsilane that provides both the regioisomers revealed that the deuterium atom is intact in the terminally vinylated compound (>98% D), while the deuterium is lost in the internally vinylated derivative (eq 6). Thus, we find it reasonable to assume that the elimination of a PdH species is an irreversible process.



(eq. 6)

Conclusion

Palladium-catalyzed vinylation of commercially available trimethylvinylsilane (**1**) is apparently a useful method for obtaining various 3-substituted 1-trimethylsilyl 1,3-dienes in a one-step procedure using either vinyl iodides or activated vinyl bromides in the presence of silver salts or, alternatively (if preferable), vinyl triflates as starting materials (eq 7). The addition of silver salts enhances the reaction rate considerably and suppresses the desilylation. Thus, under ordinary Heck reaction conditions, the desilylation is predominant and consequently **1** in these cases operates instead as an ethylene equivalent. Due to the easy access of the vinyl iodides or of triflates, and due to the simplicity of the experimental procedure, we think that the synthetic approach discussed here in many cases compares favorably with other existing methods.[3]



(eq.7)

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(18) Halide abstraction by silver triflate from arylpalladium halides has been reported: (a) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (b) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1984**, *260*, C52–54.

(19) We have verified that the inorganic precipitation in our reactions consists of silver iodide by the powder diffraction technique.

Experimental Section

Materials. Vinylic Halides. (*E,Z*)-β-Bromostyrene, 2-bromo-1-propene, (1-bromovinyl)trimethylsilane, and (*Z*)-1-bromo-2-ethoxyethylene were purchased from Fluka AG and were used as received. The following vinylic halides were prepared according to literature methods: (*E*)-methyl 3-bromopropenoate,[20] methyl 2-bromopropenoate,[21] 3-bromo-2-cyclohexen-1-one,[22] 3-iodo-2-cyclohexen-1-one,[22] (*E*)-1-iodohexene,[23] (*E*)-β-iodostyrene,[23] 2-iodohexane,[24] 1-iodocyclopentene,[25] and 1-iodocyclohexene.[25]

Vinylic Triflates. The following triflates were prepared according to literature methods:[26] cyclopentenyl triflate,[27] cyclohexenyl triflate,[27] and 6-methoxy-3,4-dihydro-1-naphthalenyl triflate.[9l] 1-[(Trimethylsilyl)ethynyl]-2,2-dimethylethenyl triflate[28] was prepared from isopropyl (trimethylsilyl)ethynyl ketone, which was generously supplied by Dr. L.-G. Wistrand.

Other Reagents. Palladium acetate (Fluka), triphenylphosphine (Fluka), triethoxyphosphine (Fluka), silver nitrate (Merck), silver triflate (Merck), dimethyl sulfoxide (Riedel), dimethylformamide (Janssen), acetonitrile (Janssen), triethylamine (Merck), and trimethylvinylsilane (Aldrich) were used as received from the commercial sources indicated. Tetrahydrofuran was distilled from sodium. *tert*-Butyllithium (Aldrich) was standardized by a doublet titration with diphenylacetic acid in THF.[29] Tri-*o*-tolyphosphine[30] and tetrakis(triphenylphosphine)palladium[31] were prepared by literature methods.

General Procedures. The NMR spectra were recorded on a Varian XL 300 instrument (300 MHz, ^{1}H; 46 MHz, ^{2}H). The ^{1}H NMR shifts are given relative to TMS in $CDCl_3$ and ^{2}H NMR shifts are given relative to TMS-d_{12} in $CHCl_3$ unless noted otherwise. Mass spectra were obtained on a Finnigan 4021 (Data System Incos 2100) gas chromatograph/mass spectrometer at 70 eV. Deuterium contents were estimated by mass spectroscopy at 16 or 70 eV. Quantitative gas chromatographic analyses were performed on a Varian 3300 instrument equipped with a (2.5 m × 2 mm) glass column of 5% OV17 on Chromosorb W. A Varian 3700 instrument was used for capillary gas chromatography on a Supelcowax 10 (30 m × 0.25 μm) column. 2,3-Dimethylnaphthalene was used as an internal standard. Column chromatography was carried out by using E. Merck silica gel 60 (0.040–0.064 mm) and pentane or pentane/ether (17:1) as eluent. All reactions in the temperature range between 80 and 100 °C were run in a 100-mL heavy-walled, thin-necked Pyrex tube, sealed with a Teflon stopcock, and with magnetic stirring. Reactions at 50 °C were run in a round-bottomed flask with magnetic stirring. Elemental analyses were performed by Dornis u. Kolbe Microanalytical Laboratory, Mülheim, West Germany. HPLC separations were performed on a LDC Consta Metric III system equipped with a RI detector (LKB 2142 refractive index detector) and a 500-mm (RP18 polygosil 5 μm) column. We thank Göran Svensson for performing the power diffraction experiment.

General Procedure for the Reaction of Vinyl Halides with Trimethylvinylsilane. Each of the reactants was dissolved or dispersed in dimethyl sulfoxide or acetonitrile (a total of 100 mL) and was added to a round-bottomed flask in the following order: palladium acetate (67 mg, 0.3 mmol), silver nitrate (1.7 g, 10 mmol), vinyl halide (10 mmol), triethylamine (3.0 g, 30 mmol), and trimethylvinylsilane (3.0 g, 30 mmol). The contents were heated and magnetically stirred for the appropriate time (see Table I). When the vinyl halide had been consumed, the mixture was allowed to cool. The contents were filtered and then poured into 100 mL of water. After extraction with ether or pentane (4 × 50 mL), the combined organic phases were washed with 50 mL of water, dried ($MgSO_4$), and evaporated. The crude product was subjected to column chromatography.

General Procedure for the Reaction of Vinyl Triflates with Trimethylvinylsilane. A mixture consisting of palladium acetate (67 mg, 0.3 mmol), vinyl triflate (10 mmol), triethylamine (3.0 g, 30 mmol), trimethylvinylsilane (3.0 g, 30 mmol), and dimethyl sulfoxide (100 mL) was heated and magnetically stirred for the appropriate time (see Table II). The mixture was cooled to room temperature, poured into water (100 mL), and treated as above.

General Procedure for the Reaction of Trimethylvinylsilane with Vinyl Boronic Acids. A mixture consisting of boronic acid (1.0 mmol), palladium acetate (1.0 mmol), triethylamine (3.0 mmol), trimethylvinylsilane (3.0 mmol), internal standard, and dimethyl sulfoxide (10 mL) was stirred at 50 °C for 3 h. Samples of 1.0 mL were collected and partitioned between pentane and water, and the organic phase was analyzed by GC.

Trimethyl(1-iodovinyl)silane. Following the literature procedure,[32] we treated trimethyl(1-bromovinyl)silane with 2.1 equiv of *t*-BuLi in THF. The anion was quenched with elemental iodine (5% excess) in THF. The crude product was chromatographed on silica to afford the desired product in 56% yield as a colorless oil: ^{1}H NMR δ 0.18 (s, 9 H), 6.68 (d, J = 1.5 Hz, 1 H), 6.74 (d, J = 1.5 Hz, 1 H); MS, m/e 226 (M^+, 20), 211 (10), 185 (65), 171 (5), 157 (5), 99 (35), 73 (100), 58 (20), and 43 (40). Anal. Calcd for $C_5H_{11}ISi$: C, 26.56; H, 4.90. Found: C, 26.20; H, 5.11. In an alternative procedure, the anion generated from the corresponding Grignard reaction in THF was quenched with iodine at 0 °C. The crude mixture was distilled to give 67% of the product, bp 65–67 °C (40 mm), contaminated with 15% of 2,3-bis(trimethylsilyl)buta-1,3-diene.

Trimethyl(1-deuteriovinyl)silane.[33] In a procedure analogous to that above, the anion generated from 18 mmol of trimethyl(1-bromovinyl)silane and 2.1 equiv of *t*-BuLi in THF was quenched with D_2O (10% excess). The resulting solution was diluted with 50 mL of pentane, washed several times with water, and dried. ^{2}H NMR of the pentane solution in chloroform (1:1) showed a singlet peak at 6.02 ppm. The deuterium content estimated by MS (M^+ – 15) was >98%.

Reaction of (*E*)-β-Iodostyrene with Trimethyl(1-deuteriovinyl)silane. According to the general procedure, a mixture of palladium acetate (0.03 mmol), silver nitrate (2.0 mmol), (*E*)-β-iodostyrene (1.0 mmol), triethylamine (3.0 mmol), DMSO (15 mL) and 15 mL of the pentane solution containing trimethyl(1-deuteriovinyl)silane (see above) were added to a Pyrex tube and stirred vigorously at 50 °C for 3 h. After the usual workup, column chromatography yielded 42% of (*E,E*)-trimethyl(1-deuterio-4-phenyl-1,3-butadienyl)silane and **14** as a 71:26 mixture. ^{2}H NMR of that mixture showed a singlet peak at 6.08 ppm (>98%, D). Assignment was based on the comparison with the chemical shifts in the corresponding ^{1}H NMR spectra. The deuterium content of the minor isomer was <5%.

(*E*)-Trimethyl[2-(cyclohex-1-en-1-yl)ethenyl]silane (2) (Table I, entry 1; Table II, entry 14): ^{1}H NMR δ 0.08 (s, 9 H), 1.54–1.71 (m, 4 H), 2.11–2.18 (m, 4 H), 5.70 (dd, J = 19.0, 0.6 Hz, 1 H), 5.81 (br s, 1 H), 6.53 (d, J = 19.0 Hz, 1 H); MS, m/e 180 (M^+, 10), 165 (30), 137 (25), 120 (5), 105 (8), 99 (11), 85 (15), 73 (60), 59 (100), 45 (25). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.55; H, 11.15.

(*E*)-Trimethyl[2-(cyclopent-1-en-1-yl)ethenyl]silane (3) (Table I, Entry 2; Table II, Entry 15). When the reaction was run according to Table I (entry 2), additional catalyst (2 mol %) and trimethylvinylsilane (2 equiv) were added after 2 and 7 h, respectively: ^{1}H NMR (C_6D_6) δ 0.14 (s, 9 H), 1.76 (quintet, J = 7.3 Hz, 2 H), 2.26–2.33 (m, 2 H), 2.38–2,44 (m, 2 H), 5.64–5.68 (m, 1 H), 5.82 (dq, J = 18.8, 1.0 Hz, 1 H), 6.94 (d, J = 18.8 Hz, 1 H); MS, m/e 166 (M^+, 20), 151 (50), 138 (12), 123 (30), 109 (8), 95 (8), 91 (8), 85 (65), 73 (40), 59 (100), 55 (20), 45 (35); ^{13}C NMR (C_6D_6, 75.4 MHz) δ –0.86, 23.48, 31.25, 33.40, 129.21, 131.53, 141.42,

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[33] Soderquist, J. A.; Hassner, A. *J. Organomet. Chem.* **1981**, *271*, 151.

145.12. Anal. Calcd for $C_{10}H_{18}Si$: C, 72.21; H, 10.91. Found: C, 72.35; H, 10.95. Irradiation at 2.30 ppm resulted in a dd (J = 18.8, 0.9 Hz) at 5.82 ppm and a quintet (J = 0.7 Hz) at 5.66 ppm. Irradiation at 2.40 ppm gave no reduction of the dq at 5.82 ppm. Furthermore, irradiation of the high-field multiplet (δ 2.30) resulted in an enhancement of the signals of the proton at 5.66 ppm, whereas saturation of the low-field (δ 2.40) multiplet resulted in an enhancement of the signals of the proton at 5.82 ppm.

(*E*)-Trimethyl[2-(cyclopent-1-en-1-yl)ethenyl]silane (3) and (*E*)-Trimethyl[2-[5-(cyclopent-1-en-1-yl)cyclopent-1-en-1-yl]ethenyl]silane (4) (Table I, Entry 3). When DMSO was used as solvent, the reaction gave 53% and 25% yields (GC) of **3** and **4** respectively, which were isolated by HPLC (CH_3CN). Compound **4**: ^{1}H NMR (C_6D_6) δ 0.13 (s, 9 H), 1.67–1.84 (m, 3 H), 1.96–2.09 (m, 1 H), 2.14–2.39 (m, 6 H), 3.71–3.75 (m, 1 H), 5.43–5.46 (m, 1 H), 5.73 (br s, 1 H), 6.07 (dq, J = 19.0, 1.0 Hz, 1 H), 6.86 (d, J = 19.0 Hz, 1 H); MS, *m/e* 232 (M^+, 5), 158 (20), 143 (5), 130 (12), 129 (8), 117 (7), 91 (7), 73 (100), 67 (10), 59 (25); ^{13}C NMR (C_6D_6, 75.4 MHz) δ −0.95, 24.16, 31.40, 32.09, 32.78 (2 C), 46.09, 124.23, 129.55, 132.49, 140.60, 146.09, 147.11; MS exact mass calcd for $C_{15}H_{24}Si$ 232.1647, found 232.1647. Structural assignment of **4** was based on the following: a DEPT experiment gave the multiplicity of the carbons. Irradiation of the proton at 3.73 ppm resulted in an enhancement of the signals of the proton at 6.07 ppm, but no reduction of signal structure. These results were compared with the irradiation experiments on **3** (see above).

(*E*)-1,3-Bis(trimethylsilyl)-1,3-butadiene (5) (Table I, Entry 4). Acetonitrile was used as solvent, and additional catalyst (2 mol %) and trimethylvinylsilane (2 equiv) were added after 2 and 7 h, respectively. The ^{1}H NMR spectrum of the isolated diene matched the spectrum previously reported.[34]

(*E*)-1,3-Bis(trimethylsilyl)-1,3-butadiene (5), 1,3,5-Tris(trimethylsilyl)-1,3-cyclohexadiene (6), and 1,3,5-Tris(trimethylsilyl)benzene (7) (Table I, Entry 5). When the reaction was run in DMSO, 55% (GC) of **5** and 35% (GC) of **6** were formed. After workup and separation by HPLC (CH_3CN), a 3:1 (NMR) mixture of **6** and **7** was obtained: ^{1}H NMR δ −0.02 (s, 9 H, **6**), 0.07 (s, 9 H, **6**), 0.08 (s, 9 H, **6**), 0.29 (s, 27 H, **7**), 1.68 (ddd, J = 9.6, 5.4, 4.6 Hz, 1 H, **6**), 2.23 (ddt, J = 16.6, 4.6, 0.8 Hz, 1 H, **6**), 2.41 (dddd, J = 16.6, 9.6, 2.7, 0.8 Hz, 1 H, **6**), 6.12–6.14 (m, 1 H, **6**), 6.16 (distorted d, J = 5.4 Hz, **6**), 7.69 (s, 3 H, **7**). Irradiation at 1.68 ppm gave a multiplet at 6.16 ppm, a dt (J = 16.6, 0.8 Hz) at 2.23 ppm, and a dq (J = 16.6, 2.7 Hz) at 2.41 ppm. Irradiation of the protons in the vinylic region rsulted in a dd (J = 9.6, 4.6 Hz) at 1.68 ppm, a dd (J = 16.6, 4.6 Hz) at 2.23 ppm, and a dd (J = 16.6, 9.6 Hz) at 2.41 ppm. Compound **7** was identified by its ^{1}H NMR spectrum, by comparison with an authentic sample prepared by a literature procedure.[35]

(*E*)-Trimethyl[2-(1-oxocyclohex-2-en-3-yl)ethenyl]silane (8) (Table I, Entries 6 and 13). This diene was prepared from 3-iodo-2-cyclohexen-1-one. The product was characterized by its ^{1}H NMR spectrum, which matched the literature spectrum.[1e] When 3-bromo-2-cyclohexen-1-one was used as starting material, completion of the reaction could not be achieved (70%, GC) even when more catalyst, silver nitrate, and trimethylvinylsilane were added and the reaction temperature was raised to 80 °C.

(*E*)-Trimethyl(3-butyl-1,3-butadienyl)silane (9) and Trimethyl(3-methyl-4-propyl-1,3-butadienyl)silane (10) (Table I, Entry 7). An inseparable mixture of **9** and **10** (ratio = 3.5:1) was obtained: ^{1}H NMR δ 0.09 (s, 9 H, **9**), 0.10 (s, 9 H, **10**), 0.90–0.95 (m, **9** and **10**), 1.29–1.51 (m, **9** and **10**), 1.81 (q, J = 1.2 Hz, 3 H, **10**), 2.15–2.25 (m, **9** and **10**), 5.03 (br s, 2 H, **9**), 5.40–5.47 (triplet of multiplets, J = 7.5 Hz, 1 H, **10**), 5.85 (doublet of multiplets, J = 18.9 Hz, 1 H, **10**), 5.88 (d, J = 19.1 Hz, 1 H, **9**), 6.54 (d, J = 19.1 Hz, 1 H, **9**), 6.97 (dd, J = 18.9, 0.9 Hz, 1 H, **10**). The spectrum of compound **9** matched the literature spectrum.[3m] The structure of **10** was based on decoupling experiments: irradiation at 1.8 ppm gave a triplet of triplets (J = 7.5, 0.8 Hz) at 5.43 ppm, and irradiation at 2.18 ppm resulted in a multiplet (J < 1 Hz) at 5.43 ppm and dd (J = 18.9, 0.9 Hz) at 5.84 ppm.

(*E,E*)-Trimethyl-1,3-octadienylsilane (11) and (*E*)-Trimethyl-1,3-octadien-2-ylsilane (12) (Table I, Entry 8). A mixture of **11** and **12** (3:1) was isolated together with 10% of three other isomers and 5% of (*E,E*)-5,7-dodecadiene (according to GC/MS analysis). The mixture was partly separated by HPLC (CH_3CN). The ^{1}H NMR spectrum matched the literature spectrum of **11**[3h] and of **12**.[3p]

(*E,E*)-Trimethyl(4-phenyl-1,3-butadienyl)silane (13) and (*E*)-Trimethyl(4-phenyl-1,3-butadien-2-yl)silane (14) (Table I, Entries 10 and 11). HPLC separation (CH_3CN/H_2O, 85:15) of the isomers gave **13**, the ^{1}H NMR spectrum of which matched the literature spectrum,[3g] and **14**: ^{1}H NMR δ 0.25 (s, 9 H), 5.51 (d, J = 3.3 Hz, 1 H), 5.87 (d, J = 2.8 Hz, 1 H), 6.61 (d, J = 16.4 Hz, 1 H), 6.92 (d, J = 16.4 Hz, 1 H), 7.20–7.44 (m, 5 H); MS, *m/e* 202 (M^+, 2), 128 (20), 73 (100), 59 (20), 45 (20). Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.96. Found: C, 76.89; H, 9.13.

(*E,E*)-Trimethyl(4-carbomethoxy-1,3-butadienyl)silane (15) and (*E*)-Trimethyl(4-carbomethoxy-1,3-butadien-2-yl)silane (16) (Table I, Entry 12). Separation of the isomers was accomplished by HPLC (CH_3CN/H_2O, 70:30). (*E,E*)-Trimethyl(4-carbomethoxy-1,3-butadienyl)silane: ^{1}H NMR δ 0.12 (s, 9 H), 3.75 (s, 3 H), 5.88 (dt, J = 15.4, 0.9 Hz, 1 H), 6.35 (dt, J = 18.3, 0.8 Hz, 1 H), 6.60 (ddd, J = 18.3, 10.4, 0.8 Hz, 1 H), 7.23 (ddd, J = 18.4, 10.4, 0.8 Hz, 1 H); MS, *m/e* 184 (M^+, 2), 169 (42), 95 (15), 89 (100), 79 (62), 75 (15), 69 (10), 59 (90), 45 (25). Anal. Calcd for $C_9H_{16}O_2Si$: C, 58.65; H, 8.75. Found: C, 58.80, H, 8.69. (*E*)-Trimethyl(4-carbomethoxy-1,3-butadien-2-yl)silane: ^{1}H NMR δ 0.20 (s, 9 H), 3.76 (s, 3 H), 5.75 (d, J = 3.0 Hz, 1 H), 5.95 (d, J = 16.1 Hz, 1 H), 6.05 (d, J = 3.0 Hz, 1 H), 7.44 (d, J = 16.1 Hz, 1 H); MS, *m/e* 184 (M^+, 3), 169 (5), 95 (5), 89 (43), 80 (70), 73 (100), 59 (40), 52 (35), 45 (40). Anal. Calcd for $C_9H_{16}O_2Si$: C, 58.65; H, 8.75. Found: C, 58.65; H, 8.64.

(*E*)-Trimethyl[2-(6-methoxy-3,4-dihydronaphthalen-1-yl)ethenyl]silane (17) (Table II, Entry 16). An inseparable mixture of **17** and two other isomers (ratio = 87:8:5) was isolated: ^{1}H NMR δ 0.14 (s, 9 H), 2.25–2.32 (m, 2 H), 2.71 (t, J = 7.6 Hz, 2 H), 3.81 (s, 3 H), 6.11 (m, 1 H), 6.22 (d, J = 19.0 Hz, 1 H), 6.70–6.81 (m, 3 H), 7.29–7.32 (m, 1 H); MS, *m/e* 258 (M^+, 50), 243 (35), 185 (45), 73 (100), 59 (50), 45 (25). Anal. Calcd for $C_{16}H_{22}OSi$: C, 74.36; H, 8.58. Found (mixture): C, 74.10; H, 8.25.

(*E*)-Trimethyl[3-[(trimethylsilyl)ethynyl]-4-methyl-1,3-pentadienyl]silane (18) (Table II, entry 17): ^{1}H NMR δ 0.10 (s, 9 H), 0.23 (s, 9 H), 1.93 (s, 3 H), 2.08 (s, 3 H), 6.25 (d, J = 18.4 Hz, 1 H), 6.78 (d, J = 18.3 Hz, 1 H); MS, *m/e* 250 (M^+, 10), 176 (8), 161 (8), 147 (20), 131 (5), 110 (6), 97 (6), 83 (8), 73 (100), 59 (15), 45 (25). Anal. Calcd for $C_{14}H_{26}Si_2$: C, 67.12; H, 10.46. Found: C, 67.00; H, 10.20.

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Registry No. 1, 754-05-2; **2**, 116103-21-0; **3**, 116103-22-1; **4**, 116103-23-2; **5**, 22500-95-4; **6**, 116103-24-3; **7**, 5624-60-2; **8**, 84132-55-8; **9**, 91158-86-0; **10**, 116103-25-4; **11**, 106335-82-4; **12**, 111379-49-8; **13**, 70960-88-2; **14**, 114701-81-4; **15**, 116103-26-5; **16**, 116103-27-6; **17**, 116103-28-7; **18**, 116103-29-8; 1-iodocyclohexene, 17497-53-9; 1-iodocyclopentene, 17497-52-8; trimethyl(1-iodovinyl)silane, 116103-20-9; 3-iodo-2-cyclohexen-1-one, 56671-82-0; 2-iodo-1-hexene, 54145-19-6; (*E*)-1-iodo-1-hexene, 16644-98-7; [(*E*)-1-hexen-1-yl)boronic acid, 42599-18-8; (*E*)-β-iodostyrene, 42599-24-6; [(*E*)-2-phenylethenyl)boronic acid, 6783-05-7; methyl (*E*)-3-bromo-2-propenoate, 6213-87-2; 3-bromo-2-cyclohexen-1-one, 56671-81-9; (*E,E*)-5,7-dodecadiene, 30651-68-4; 1-cyclohexenyl triflate, 28075-50-5; 1-cyclopentenyl triflate, 28075-49-2; 6-methoxy-3,4-dihydro-1-naphthalenyl triflate, 115375-59-2; 1-[(trimethylsilyl)ethynyl]-2,2-dimethylethenyl triflate, 71451-04-2; trimethyl(1-bromovinyl)silane, 13683-41-5; 2,3-bis(trimethylsilyl)buta-1,3-diene, 22472-36-2; trimethyl(1-deuteriovinyl)silane, 79678-00-5; (*E,E*)-trimethyl(1-deuterio-4-phenyl-1,3-butadienyl)silane, 116103-30-1.

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