A novel selective route to 1,1-bis(silyl)-1-alkenenes has been developed. Sequential one-pot silylative coupling exocyclization of 1,2-bis(dimethylvinylsiloxy)ethane followed by the reaction with Grignard reagents leads to the desired 1,1-bis(silyl)ethenes, which are then efficiently coupled in the presence of silver nitrate and palladium acetate with aryl or alkenyl iodides to give the corresponding 1,1-bis(silyl)-2-arylethenes or 1,1,4-trisubstituted 1,3-butenadienes with high yield.

1,1-Dimetalated-1-alkenenes constitute an important class of organometallic reagents which are currently widely used as potential intermediates in the organic and organometallic syntheses. Among the most notable and commonly employed gem-digematinetallenes, the 1,1-bis(silyl)-1-alkenenes are of unique importance. Their use as precursors for the preparation of ketones as well as a variety of important organosilicon intermediates such as acylsilanes, epoxysilanes, 1-halovinylsilanes, silyl enol ethers, (E)-alkenylsilanes, silyl enol acetates, etc., stimulates interest in their synthetic availability (Scheme 1). Silylated 1,3-dienes are also well established as useful intermediates in regio- and stereoselective organic synthesis due to their high reactivity and stereospecificity toward various dienophiles and electrophiles.

Since geminally silylated alkenes are versatile reagents in organic and organosilicon synthesis, considerable effort has been made to find new routes for the preparation of these compounds and for their selective reactions with a range of electrophiles. Conventional approaches to 1,1-bis(silyl)-1-alkenenes involve multistep reactions of carbonyl compounds with commercially unavailable dihalodisilylmethanes. Hodgson and co-workers have developed a chromium(II)-mediated reaction of aldehydes with dibromodisilylmethanes. Oshima et al. have reported a synthesis of 1,1-bis(silyl)-1-alkenenes from ketones or acyl chlorides and 1,1-bis(silyl)-substituted allylic copper derivatives, obtained via a copper(I)-mediated vinylation of chlorodisilyllithium. The reaction of dibromodisilylmethanes with lithium trialkylmagnesates or R₂SiCH₂MgCl followed by dehydrobromination of the resulting 1-bromo-1,1-diisilylalkanes provides an alternative route to 1,1-bis(silyl)-1-alkenenes. However, the application of these methods is limited by complicated synthetic procedures involving the use of harmful starting materials and highly reactive organolithium compounds.

The palladium-catalyzed reaction of aryl and alkenyl halides with alkenes (the Heck reaction) is regarded as one of the most versatile tools in modern synthetic chemistry and has great potential for industrial applications. Although this particular reaction can in principle be applied to any kind of alkene, it is already known that there are significant difficulties with the Heck coupling of vinylsilanes. Palladium-catalyzed reaction of aryl and alkenyl halides with vinylsilanes under typical Heck coupling conditions have been described leading mostly to styrene derivatives as a result of carbon–silicon bond cleavage. Itami et al. have reported that the catalyst-directing 2-piryld group on silicon enable the Heck coupling of vinylsilanes with...
aryl halides by the agency of a strong complex-induced proximity effect. However, in this reaction, biaryls are the major products reported procedure. This added. However, in this reaction, biaryls are the major products considerably. A mechanistic study has shown that silver ions not only act as an iodide abstractor but also facilitate the oxidative addition of catalytically active Pd(0) species by attachment to the iodo substituent and also by formation of an electron donor-acceptor complex with the armonic ring.

Although there are several reports on the successful arylation and olefination of simple vinylsilanes, the application of the Heck reaction to 1,1-bis(silyl)ethenes lags far behind mainly due to the complexity of their synthesis. During the course of our recent studies on the silylative coupling cyclization of divinyl-substituted organosilicon compounds we have developed new simple and efficient methods for the synthesis of alkyl-, aryl-, alkenyl-, or alkoxysubstituted 1,1-bis(silyl)ethenes using cyclic silyl ether or cyclic silylamine selectively obtained via ruthenium-catalyzed silylative coupling exo-cyclization of divinyl-substituted monomers, followed by their reaction with Grignard reagents or alcohols.

Herein, we report a new facile and selective two-step protocol for synthesis of 1,1-bis(silyl)-2-arylenes and 1,1-bis(silyl)-1,3-butadienes from easily available 1,2-bis(dimethylvinylsiloxy)ethane. Our synthetic methodology involves a one-pot reaction sequence—ruthenium hydride complex-catalyzed silylative coupling exo-cyclization followed by the reaction with Grignard reagents or alcohols. In 1,1-bis(trimethylsilyl)ethene 1 and 1,1-bis(dimethylphenylsilyl)ethene 2 we prepared the one pot implementation of our recently reported procedure. This facile synthetic methodology involved consecutive ruthenium-catalyzed silylative coupling cyclization of 1,2-bis(dimethylvinylsiloxy)ethane and the reaction of the resulting cyclic silyl ether with methylmagnesium iodide or phenylmagnesium bromide without isolation of the cyclic bis(silyl) intermediate (Scheme 2).

At the outset, we began by establishing the conditions for the Heck arylation of 1,1-bis(trimethylsilyl)ethene 1 with iodobenzene. In early experiments, we investigated the influence of phosphine, base, and the solvent on the selectivity of the silver nitrate-mediated reaction with commonly used catalysts such as Pd(OAc)2, Pd(db)2, or Pd2(db)2. The reactions were performed at 60 or 80 °C in DMF, THF, toluene, or MeCN in the presence of a ratio 1/2 of [Pd]/phosphine as a catalyst (3 mol %, 6 mol %) and triethylamine as a base. In the presence of the dibenzylideneacetone palladium/phosphine (PPh3, P(2-furyl)3, P(4-Tol)) catalytic system, the Heck-coupled product was obtained with moderate yield, but the reaction was not selective and the formation of a large amount of desilylation products (1-phenyl-1-(trimethylsilyl)ethene and stilbene) was also observed. Disappointingly low selectivities were also obtained using potassium carbonate, sodium acetate, or potassium fluoride. The highest selectivity in terms of the formation of arylated 1,1-bis(trimethylsilyl)ethene was observed using an excess of triethylamine and palladium(II) acetate/triethylphosphine as catalyst. After several attempts, we found that the reaction of compound 1 (1 equiv) with 1 equiv of aryl iodide, 1 equiv of AgNO3, and 2 equiv of Et3N, in the presence of 3 mol % of Pd(OAc)2 and 6 mol % of PPh3, conducted in dry acetonitrile at 60 °C for 2 h exclusively afforded the corresponding 1,1-bis(trimethylsilyl)-2-arylene in excellent yield (compounds 3a-7a, Table 1). Similarly to the compound 1, the application of 1,1-bis(dimethylphenylsilyl)ethene 2 under analogous conditions also gave the Heck coupled products with slightly lower yields (compounds 3b-8a, Table 1); however, this particular reaction had to be carried out for a longer time (4-6 h). To our surprise, in the cases examined, the only products detected in the reaction mixture (using GC-MS method) were the desired β-aryl-substituted 1,1-bis(silyl)ethenes 3-8, which clearly signifies the high reactivity of 1,1-bis(silyl)ethenes 1 and 2 toward Heck reaction. Thus, the noteworthy features of these processes are that the formation of styrene and stilbene derivatives (via desilylation) was completely suppressed and the formation of biaryls (by homocoupling of the aryl iodides) was not observed. Moreover, the Heck coupling occurred under mild conditions with a wide array of electronically (similar reaction rates were obtained with electron-rich and electron-poor aryl iodides) and structurally diverse aryl iodides.

Having established an efficient protocol for the Heck coupling of 1,1-bis(silyl)ethenes 1 and 2 with aryl iodides, we subsequently investigated the synthesis of synthetically useful silylated 1,3-diene frameworks by means of coupling between 1 with selected alkenyl iodides. Two stereodefined alkenyl iodides, (E)-β-iodostyrene and (Z)-ethyl 2-iodopropenoate, have been selected for testing the activity of compound 1 in the alkenylation process. Unfortunately, under the identical reaction conditions to those applied for the arylation process (Pd(OAc)2, PPh3, acetonitrile, 60 °C), silver nitrate-mediated Heck coupling did not take place when alkenyl iodides were used instead of aryl iodides. After several attempts, we found that the palladium-catalyzed (3 mol % of Pd(OAc)2 and 6 mol % of PPh3) alkenylation of 1,1-bis(silyl)ethene 1 successfully proceeded in DMSO to give coupling products 9 and 10 in moderate yield (Table 1, entries 11-12); however, the reaction required a considerably higher temperature (100 °C) and longer reaction time (24 h). It is worth noting that under these optimized conditions stereospecific products (E,E)-1,1-bis(trimethylsilyl)-4-phenylbuta-1,3-diene 9 and (Z)-Ethyl 5,5-bis-(trimethylsilyl)-penta-2,4-dienoate 10 were exclusively formed. GC-MS analy-
sis of the byproducts of the reaction discussed revealed the presence of a significant amount of alkenyl iodide coupling products (1,4-diphenyl-1,3-butadiene (18%) and diethyl hexa-2,4-dienedioate isomers (38%) respectively). Although they can be easily separated by column chromatography, their formation limited the yields of 9 and 10 considerably. All preparative results are summarized in Table 1.

In conclusion, we have described a novel and efficient protocol for the synthesis of 1,1-bis(silyl)-2-arylethenes as well as 1,1-bis(silyl)-1,3-butadienes from easily available starting materials using the following sequential procedure: silylative coupling—Grignard reagent treatment—Heck coupling. Other-wise difficult to synthesize compounds were exclusively (arylation) or predominantly (alkenylation) obtained via silver nitrate-mediated and palladium-catalyzed Heck-type coupling of 1,1-bis(silyl)ethenes with aryl and alkenyl iodides. Due to the mildness and simplicity of the experimental procedure and the tolerability of a wide range of substituents in the aryl group, this particular method compares favorably with other accessible methods for the preparation of these kinds of organosilicon derivatives.

Experimental Section

One-Pot Procedure for the Synthesis of 1,1-Bis(dimethylsilyl)-ethenes. The glass reactor (50 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser and argon bubbling tube) was evacuated and flushed with argon. 1,2-Bis(dimethylvinylsiloxyl)ethane (5.00 g, 0.217 mol) and [RuHCl(CO)(PPh3)3] (0.21 g, 0.022 mmol) were added to the reactor. The reaction mixture was heated under the flow of argon for 2 h at 120 °C with stirring. After the mixture was cooled to room temperature, a 1 M solution of the corresponding Grignard reagent in THF was added dropwise (molar ratio 1,2-bis(dimethylvinylsiloxyl)ethane/Grignard reagent was 1:3). The reaction mixture was stirred under argon at 65 °C for 18 h. After the reaction was complete, the excess amount of the Grignard reagent was quenched by adding MeOH and pentane, the suspended salt was filtered off, and the volatiles...
were evaporated in vacuo. After evaporation, the crude product was chromatographed on silica gel and distilled under reduced pressure to afford the analytically pure product (yield: compound 1 (72%), compound 2 (80%)).

**Representative Procedure for the Synthesis of 1,1-Bis(silyl)-2-arylethenes (3–8).** A mixture consisting of 33.50 mg (0.15 mmol) of palladium(II) acetate, 78.60 mg (0.30 mmol) of triphenylphosphine, 0.85 g of silver nitrate (5 mmol), 5 mmol of aryl iodide, 5 mmol of 1,1-bis(silyl)ethene 1 or 2, 1.40 mL (10 mmol) of triethylamine, and 10 mL of acetonitrile was placed in 50 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar and reflux condenser. The suspension was heated in an oil bath at 60 °C for the appropriate time (see Table 1). After being cooled to room temperature, the reaction mixture was added to water (50 mL) and extracted twice with 30 mL of pentane. The combined organic layers were dried (MgSO₄), and the crude product obtained was then purified by column chromatography (silica gel/pentane) to give the corresponding 1,1-bis(silyl)-2-arylethene.

**Representative Procedure for the Synthesis of 1,1-Bis(silyl)-1,3-dienes (9–10).** A mixture consisting of 26.80 mg (0.12 mmol) of palladium(II) acetate, 62.80 mg (0.24 mmol) of triphenylphosphine, 0.68 g of silver nitrate (4 mmol), 4 mmol of alkenyl iodide, 4 mmol of 1,1-bis(silyl)ethene 1 or 2, 1.12 mL (8 mmol) of triethylamine, and 10 mL of freshly distilled DMSO was placed in a 50 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar and reflux condenser. The suspension was heated in an oil bath at 100 °C for 24 h. The reaction mixture was then poured into 100 mL of water and extracted with pentane (2 × 50 mL). The combined organic layers were dried (MgSO₄) and the crude product obtained was then purified by column chromatography (silica gel/pentane) to give the corresponding 1,1-bis(silyl)-1,3-butadiene.

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**Supporting Information Available:** Detailed experimental procedures and characterization data of the compounds prepared in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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