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Silylative Coupling of Olefins with Vinylsilanes in the Synthesis of π-Conjugated Double Bond Systems

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Dedicated to Professor Mieczysław Mąkosza on the occasion of his 75th birthday

Keywords: Silylative coupling / Arylvinyl derivatives / Cross-coupling / Halogenation / Desilylative coupling / Silanes

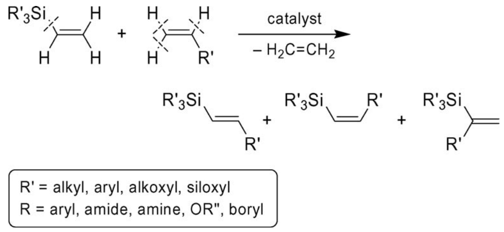
The design and development of highly efficient and selective methods for the synthesis of π-conjugated arylvinyl derivatives, based on sequential catalytic reactions of organometallic reagents, have been the subject of extensive study because of their versatile application in organic synthesis and materials science. The silylative coupling of olefins with vinyl-substituted silicon compounds represents one of the most efficient and selective methods for the synthesis of alkenylsilanes, which are particularly attractive scaffolds for further transformations, including transition-metal-catalysed cross-coupling with organic halides or substitution with organic and inorganic electrophiles. The microreview highlights recent developments in sequential synthetic strategies including ruthenium-catalysed silylative coupling followed by desilylative cross-coupling and halogenation, leading to stereodefined organic derivatives containing arylene-vinylene units widely applied as fine chemicals, functional materials or unsaturated building blocks in organic synthesis.

Introduction

Vinylsilicon compounds are a class of organosilicon reagents commonly used in organic synthesis. Much of the impetus behind the growing relevance of organosilicon compounds arises from the successful stereospecific palladium-catalysed cross-coupling or halodesilylation strategies developed for these useful organometallic reagents in the last three decades. Silicon-based cross-coupling (Hiyama coupling) has achieved significant importance in synthetic organic chemistry as a reliable alternative to the Suzuki (boron), Stille (tin) and Negishi (zinc) couplings, due to the selective reactivity, stability and non-toxicity associated with organosilicon compounds.[1]

Many efficient stereo- and regioselective methodologies for the synthesis of vinylsilanes involve classical stoichiometric routes from organometallic reagents or, recently, TM-catalysed transformations of alkynes, silylalkynes, alkenes and – in particular – terminal vinylsilanes.[2]

Of the available methods for preparation of stereodefined alkenylsilanes, transition-metal-catalysed silylative coupling of functionalized olefins with vinylsilanes (also called trans-silylation) is one of the most direct, flexible and powerful approaches (Scheme 1).



Scheme 1. Silylative couplings of olefins with vinylsilanes.

The reactions take place in the presence of complexes that contain or generate M–H and M–Si bonds (where M = Ru, Rh, Co, Ir). The mechanism of the process proposed for the Ru complexes by Wakatsuki[3] and corrected by our group,[4] and also for other metal complexes such as Rh,[5] Co[6] and Ir,[7] proceeds by insertion of vinylsilane into the M–H bond and β-Si transfer to the metal with elimination of ethylene to generate the M–Si species, followed by insertion of alkene and β-H transfer to the metal with elimination of the substituted vinylsilane (Scheme 2).

Detailed mechanisms of silylative coupling of functionalized alkenes such as styrene, vinyl alkyl ethers, vinylamides and other olefins, catalysed predominantly by ruthenium complexes, as well as all synthetic aspects of these processes, have subsequently been presented.[8]

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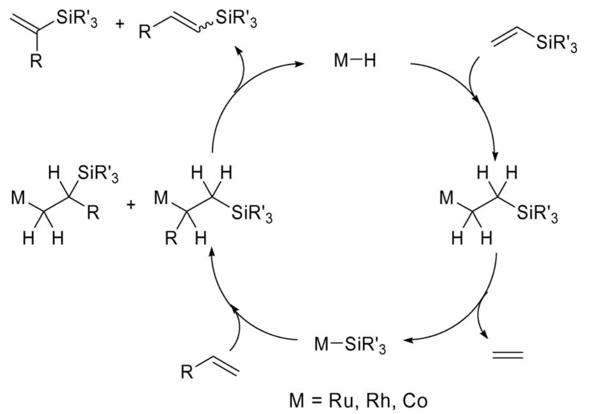

Scheme 2. Silylative coupling mechanism.

Silylative coupling appeared to be a valuable step in combination with subsequent desilylation reactions such as Hiyama cross-coupling and halodesilylation to provide highly conjugated π-electron compounds such as stilbenes or aryl-substituted polyenes. These have gained a lot of attention because of their wide range of biological activity and potential therapeutic value.[9] Some of them, such as stilbenoids, have been found in a number of plant species, especially in medicinal plants and food products,[10] and display certain biological activities including anti-inflamatory or antioxidative properties, radical scavenging activity, neuroprotection, antiviral activity, anticarcinogenic properties and antifungal effects.[11]

The conjugated polyenes are also essential in functional materials such as organic fluorescent probes, electroluminescent devices and nonlinear optical materials.[12] Of the available methods for preparation of π-conjugated systems, the transition-metal-catalysed processes utilizing C–C or C=C bond-formation reactions are the most convenient and powerful approaches.[13] However, although there are a number of synthetic methods for stilbenoids,[14] some of them suffer from low selectivities, so development of a more general, convenient and selective preparative method has become an important task. The growing interest in the development of sequential processes including silylative coupling as the initial step stems from the potential to assemble complex molecules from simple starting materials (functionalized alkenes) through organosilicon intermediates in a convergent and atom-economical manner.

Sequential Silylative Coupling/Desilylative Coupling in the Synthesis of Stilbenes

One of the most promising methods for the synthesis of stilbenes with different kinds of substituents is sequential ruthenium-catalysed silylative coupling and palladium-catalysed desilylative coupling of such obtained organosilanes with iodoarenes activated by a nucleophilic promoter (Hiyama coupling).[15] Hiyama coupling has been successfully used for synthesis of (*E*)- and (Z)-stilbenes[16] and of mono-

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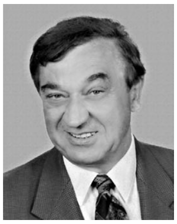

Professor Bogdan Marciniec received his M.Sc. (1963), Ph.D. (1970) and D.Sc. (1975) from the Adam Mickiewicz University, Poznan, Poland. Member of the Polish Academy of Sciences (1994). Head of the Department of Organometallic Chemistry (1987), President of the Adam Mickiewicz University (1988/1990), Director of the Center of Advanced Technologies (2006). He was a postdoctoral associate with Prof. R. C. Schowen, Kansas University (1970/1971). His research activity is focused on organosilicon chemistry and catalysis by organometallic compounds and the synthesis and catalytic reactions of substituted silanes and (poly)siloxanes, such as hydrosilylation of C=C and C≡C bonds, cross-metathesis and silylative coupling of olefins with vinylsilicon compounds. Activation of =C–H and ≡C–H bonds by M–Si, (silicometallics) as well as by M–B, M–Ge, M–Sn (general inorganometallics) and M–H complexes (where M = Ru, Rh, Ir, Co, Fe) has been another interest, leading to new organometallic reagents for organic and asymmetric synthesis, as well as to precursors of new materials. He is an author and co-author of 310 publications and 24 book chapters [e.g., Handbook of Metathesis (Wiley-VCH, 2003), Encyclopedia of Catalysis (J. Wiley & Sons, Inc., 2003), Applied Homogeneous Catalysis with Organometallic Compounds (Wiley-VCH, 2002)], as well as editor and co-author of 15 books, inter alia "Comprehensive Handbook on Hydrosilylation" (Pergamon Press, 1993) and "Hydrosilylation – A Comprehensive Review on Recent Advances (Springer, 2009). Professor Marciniec was awarded the Prime Ministry Award (2001) and the J. Sniadecki Medal of the Polish Chemical Society (2003) for outstanding achievements in chemistry. He is or has been a member of the editorial boards of such journals as Organometallics, Applied Organometallic Chemistry, Clean Products & Processes, ChemCatChem. and the Encyclopedia Britannica (Polish Edition).

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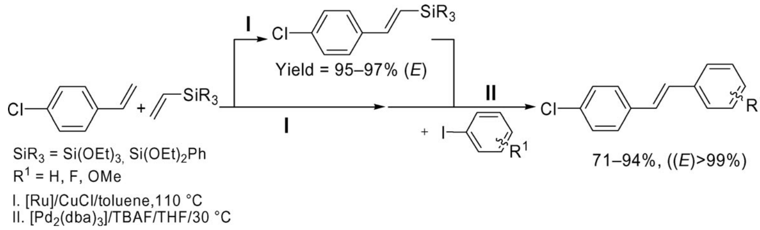


Scheme 3. Synthesis of unsymmetrical (*E*)-4-chlorostilbenes.

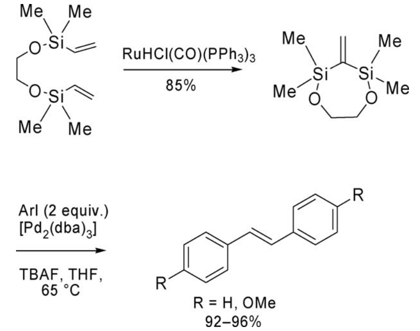
substituted (*E*)-stilbenes with electron-donating or electron-withdrawing groups.[16c–16f]

Treatment of a mixture of diethoxyphenyl- or triethoxyvinylsilane and 4-chlorostyrene in the presence of the [RuHCl(CO)(PPh$_3$)$_3$] catalyst (1 mol-%) gives rise to evolution of ethylene and selective formation of (*E*)-1-(*p*-chlorophenyl)-2-(silyl)ethenes (Scheme 3, path I).[15]

In the next step, 4-chlorostyryltriethoxy-(or diethoxyphenyl-)silanes were applied in the synthesis of chlorostilbenes through palladium-catalysed [Pd$_2$(dba)$_3$] Hiyama coupling with aryl iodides (Scheme 3, path II). This reaction leads to selective formation of the corresponding (*E*)-4-chlorostilbenes.[15]

Unsymmetrical substituted stilbenoids were also successfully obtained in “one-pot” fashion through silylative coupling and desilylative coupling (Scheme 3, 77–94% yields).[15] The unique feature of this methodology, securing its advantage over the other catalytic methods, is that the stereochemistry of this process can be controlled during the initial step, because the subsequent Hiyama coupling proceeds with retention of the configuration and allows the formation of stereodefined products. The availability of the starting materials, simplicity of the experimental technique and the potential for mild reaction conditions are favourable features of this new catalytic approach to the synthesis of (*E*)-4-halostilbene derivatives.

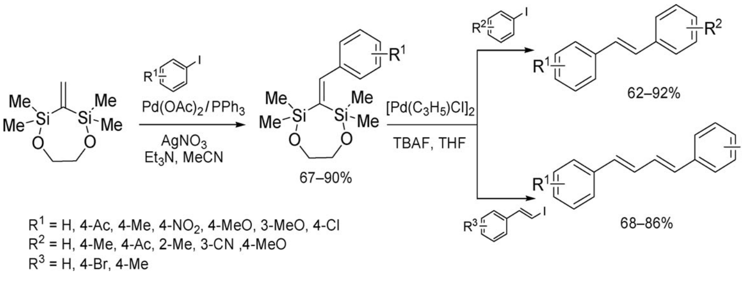
The cyclic 1,1-bis(silyl)ethene derivative 2,2,4,4-tetramethyl-1,5-dioxa-3-methylene-2,4-disilacycloheptane (Scheme 4) – easily prepared by ruthenium-catalysed silylative coupling *exo*-cyclization of silylated ethylene glycol[17] – exclusively forms symmetrical (*E*)-stilbenes (instead of the expected 1,1-diarylethenes) with perfect stereoselectivity and almost quantitative yield on treatment with aryl iodides (2 equiv.) under standard cross-coupling conditions ([Pd$_2$(dba)$_3$] catalyst and TBAF) as a result of simultaneous *ipso*- and *cine*-substitution.[18] A bis(silyl)alkene double bond can thus be very efficiently grafted into an aromatic structure, offering the potential to construct (*E*)-stilbene and polyene derivatives.



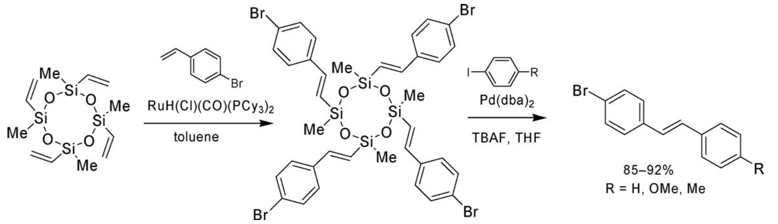
Scheme 4. Synthesis of symmetrical (*E*)-stilbenes.

Application of the cyclic 1,1-bis(silyl)ethene derivative as a platform for the iterative installation of aryl groups onto the C=C core by means of sequential palladium-catalysed Heck arylation and Hiyama cross-coupling reactions leads to stereoselective synthesis of unsymmetrically functionalized (*E*)-stilbenes and (*E*,*E*)-1,4-diaryl-substituted buta-1,3-dienes (Scheme 5).[19] The noteworthy features of these processes are that the formation of styrene, silylstyrene and symmetrical stilbene derivatives (through desilylation) was completely suppressed, and that no formation of biaryls (by homocoupling of the aryl iodides) was observed. Moreover, both Heck and Hiyama 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.

The combination of ruthenium-catalysed silylative coupling and the palladium-catalysed Hiyama coupling processes with tetravinylcyclotetrasiloxane (Scheme 6) as a supporting reagent also leads to the stereoselective synthesis of



Scheme 5. Synthesis of unsymmetrical (*E*)-stilbenes and (*E*,*E*)-1,4-diarylbuta-1,3-dienes.

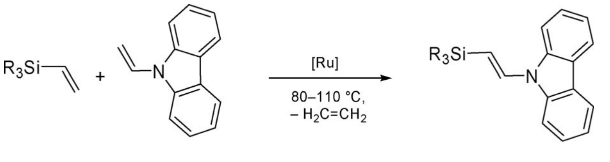


Scheme 6. Synthesis of unsymmetrical (*E*)-4-bromostilbenes.

(*E*)-stilbene derivatives in high yields.[20] Silylative coupling of tetravinylcyclotetrasiloxane with 4-bromostyrene yielded 1,3,5,7-tetrakis[(*E*)-4-bromostyryl]-1,3,5,7-tetramethylcyclotetrasiloxane, which then could be coupled with *p*-substituted aryl iodides in the presence of a [Pd(dba)$_2$] catalyst to give unsymmetrical (*E*)-4-bromostilbenes.[20]

Sequential Silylative Coupling/Desilylative Coupling in the Synthesis of (*E*)-9-Styrylcarbazoles

Carbazole derivatives with various substituents have been extensively studied, particularly because this class of compound is of great interest both for pharmacological applications and in molecular electronics. These compounds play a very important role in electroactive and photoactive materials and are also considered potential candidates for electronic devices. A particular feature of the condensed aromatic rings in the carbazole system is their ability to π-stack, which contributes to their binding affinity in macromolecules and gives rise to molecular ordering through self assembly in the solid state. Compounds possessing π-conjugated systems are widely used as good hole-transporting materials in polymeric light-emitting diodes (PLEDs) as an organic light-emitting diodes (OLEDs). Carbazole derivatives in particular are very attractive, their physicochemical properties being highly dependent on *N*-substituted hydrophilic or hydrophobic chains.[21] *N*-Arylvinylcarbazoles can be obtained by Heck arylation of *N*-vinylcarbazole, but the main drawback found for this kind of reaction is in the control of the α- and β-regioselectivity, due to the competition of cationic and neutral mechanisms in electron-rich alkenes. One of the most interesting methods for the selective functionalization of the carbazole system is sequential silylative coupling of *N*-vinylcarbazole either with vinyl-substituted silanes or with disiloxane and further catalytic transformation through Hiyama coupling with iodoarenes.[22–23] The starting *N*-silylvinylcarbazole derivatives were prepared by silylative coupling of commercially available 9-vinylcarbazole and vinyltriethoxysilane or divinyltetramethyldisiloxane in the presence of the ruthenium complex [RuH(Cl)(CO)(PCy$_3$)$_3$][22] (1 mol-%) in toluene. Under optimal conditions, the (*E*)-(silyl)(carbazyl)ethene shown in Scheme 7 was isolated successfully as the main product (accompanied by traces of vinylsilane homocoupling product).

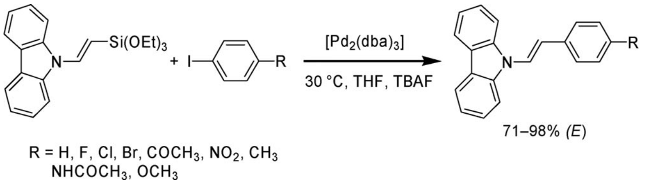


Scheme 7. Synthesis of (*E*)-*N*-silylvinylcarbazoles.

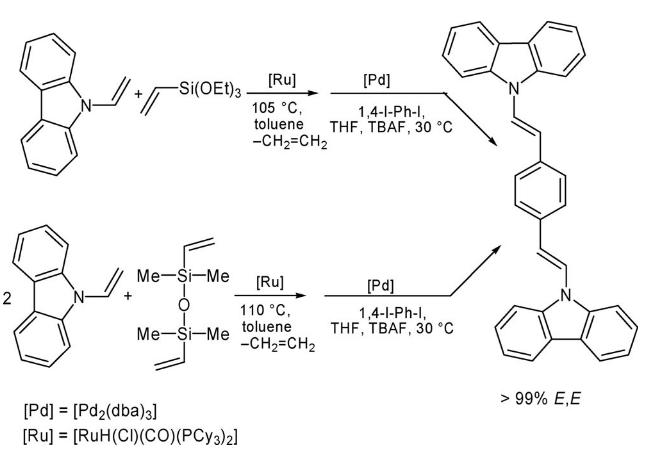
Unlike the ruthenium-hydride complex, the first-generation Grubbs catalyst is completely inactive in this reaction, whereas the second-generation Grubbs catalyst is effective but gives the product in only 35% yield.[22]

(*E*)-9-[2-(Triethoxysilyl)ethenyl]-9*H*-carbazole (Scheme 8), obtained through silylative coupling in the presence of the Pd catalyst [Pd$_2$(dba)$_3$], undergoes cross-coupling (Hiyama coupling) reactions to give *N*-arylvinylcarbazole derivatives exclusively.[22–23]

Only 4-iodoaniline did not undergo the palladium-catalysed cross-coupling reaction, even at elevated temperatures. This compound probably reacts with the palladium com-



Scheme 8. Synthesis of *N*-arylvinylcarbazoles.



Scheme 9. Synthesis of 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl)vinyl]benzene.

plex through nitrogen coordination, inhibiting further transformations.[23]

The use of 1,4-diiodobenzene in the catalytic transformation described above (silylative coupling – desilylative coupling) allows access to 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl)vinyl]benzene in excellent yield (92 %, Scheme 9).[23]

Sequential silylative coupling and desilylative coupling also allow the synthesis of 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl)-vinyl]benzene in "one-pot" fashion without isolation of the intermediate product.[23]

Synthesis of Bis[(*E*)-4-halostyryl]arenes

Stilbenoid compounds with extended π-systems show interesting photophysical and photochemical properties and are therefore suited for various applications in materials science.[12] Because of the similarities of the basic structure and interesting photophysical properties of bis(halostyryl)arenes to those of poly(phenylenevinylene)s, they have attracted significant attention as potential unsaturated monomeric building blocks in polymer synthesis.[24] Symmetrical derivatives of 1,4-distyrylbenzene serve as disperse optical brightening agents and can be used as cores of stilbenoid dendrimers.[25]

In an initial experiment, 1,4-bis[(*E*)-4-bromostyryl]benzene was obtained through sequential silylative cross-coupling between vinylpentamethyldisiloxane and 4-bromostyrene in the presence of the ruthenium complex [RuHCl(CO)(PPh$_3$)$_3$] as a catalyst (Scheme 10) and desilylative coupling of the obtained (*E*)-1-(4-bromophenyl)-2-(pentamethyldisiloxane)ethene with 1,4-diiodobenzene in the presence of a palladium catalyst.[26]

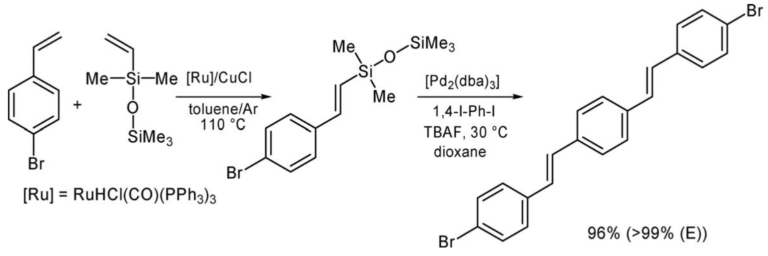
Bis[(*E*)-4-halostyryl]arenes were obtained through sequential silylative coupling of divinyltetramethyldisiloxane with 4-halostyrenes (Scheme 11), followed by desilylative coupling of the bis(4-halostyryl)tetramethyldisiloxanes in the presence of a palladium catalyst. Twofold excesses of 4-halostyrene relative to divinyltetramethyldisiloxane were enough to achieve complete silylative coupling of both vinyl groups, and homo-polymerization of halostyrene was still not observed.[26]

These one-pot reactions afforded a wide range of symmetrical bis[(*E*)-4-halostyryl]arenes with high yields (43–98 %) and stereoselectivities (>99 %).[26] The availability of the starting materials, simplicity of the experimental technique and the mild reaction conditions are favourable features of this new catalytic approach to the synthesis of 1,4-bis[(*E*)-4-halostyryl]arenes. The Suzuki and Heck reactions also give similar products, but need more specialised, sometimes very expensive, substrates than the one-pot silylative-desilylative coupling reaction.

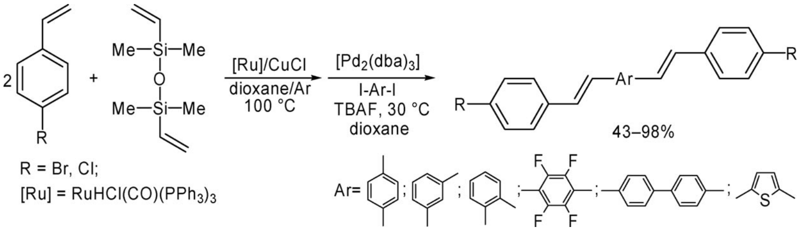
Sequential Silylative Coupling/Desilylative Coupling in the Synthesis of Stilbenoid Dendrimer Cores

The next class of compounds synthesized in sequential silylative coupling/desilylative coupling reactions were dendrimers with polyconjugated branches, which represent an important group in this class of materials, of interest because of their electrical, optical, nonlinear optical, electroluminescent and photophysical properties. Such compounds have been successfully used, for example, as charge-transporting and light-emitting materials.[12]

In the first step, the unsaturated organosilicon precursors – [bis(4-halostyryl)tetramethyldisiloxanes] – were synthesized by ruthenium-hydride-catalysed silylative coupling of 1,3-divinyltetramethyldisiloxane with 4-halostyrenes (Scheme 12). The reaction mixture was then treated with the appropriate tri(or tetra)halobenzene under standard Hiyama cross-coupling conditions.[27] A twofold excess of the 4-halostyrene relative to divinyltetramethyldisiloxane (per silyl group) was found to be enough for completion of the

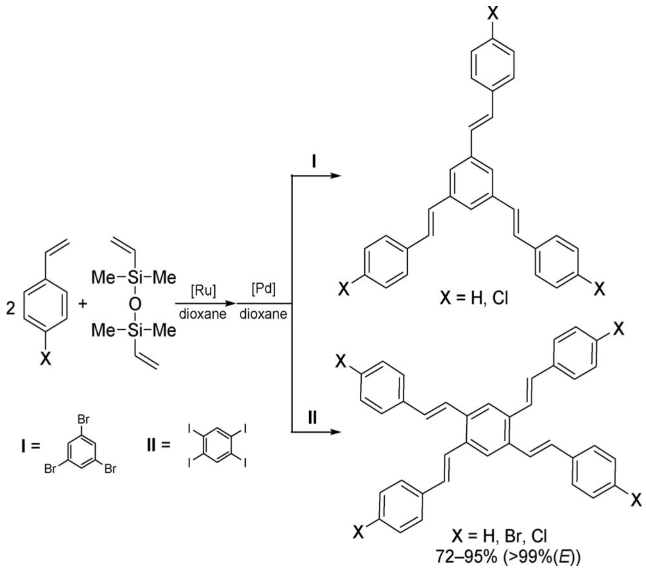


Scheme 10. Synthesis of 1,4-bis[(*E*)-4-bromostyryl]benzene.



Scheme 11. Synthesis of 1,4-bis[(*E*)-4-halostyryl]arenes.

silylative coupling reaction of both vinyl groups, and no polymerization of halostyrene was observed under these conditions.



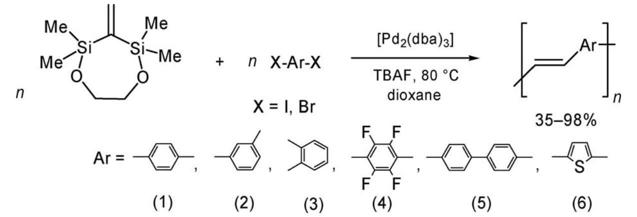
Scheme 12. Synthesis of stilbenoid dendrimer cores.

These optimal conditions provided very high yields (72–95%) and stereoselectivities (>99%) when applied to the one-pot syntheses of 1,3,5-tris[(*E*)-4-chlorostyryl]benzene or 1,2,4,5-tetrakis[(*E*)-4-halostyryl]benzenes (Scheme 12).

Notably, the yields were only slightly lower than those obtained in the two-step process with isolation of 1,3-bis[(*E*)-4-halostyryl]disiloxanes.[27] Unfortunately, a mixture of linear and branched polymers was isolated from 1,3,5-tribromobenzene and 4-bromostyrene under standard desilylative coupling conditions, due to the presence of bromine substituents in both substrates.[27]

Sequential Silylative Coupling/Desilylative Coupling in the Synthesis of Poly(arylenevinylene)s (PAVs)

Poly(arylenevinylene)s (PAVs) constitute another group of π-conjugated polymers that have attracted considerable interest because of their potential applications in electronic and optoelectronic devices, including in light-emitting diodes, solar cells, plastic lasers, fluorescent sensors, rechargeable batteries, field-effect transistors etc.[28] Although there are many reports on successful applications of the Hiyama coupling in the synthesis of molecular π-conjugated organic frameworks, the potential for the use of this particular method for the synthesis of arylene-vinylene oligomers and polymers has not so far been fully exploited.[29] The use of the cyclic 1,1-bis(silyl)ethene derivative 2,2,4,4-tetramethyl-1,5-dioxa-3-methylene-2,4-disilacycloheptane[17] (Scheme 13) as a double bond equivalent in reactions with appropriate diiodo- or dibromoarenes under standard cross-coupling conditions ([$Pd_2(dba)_3$], TBAF) provides almost quantitative yields of the expected poly(arylenevinylene)s (PAVs).[18]

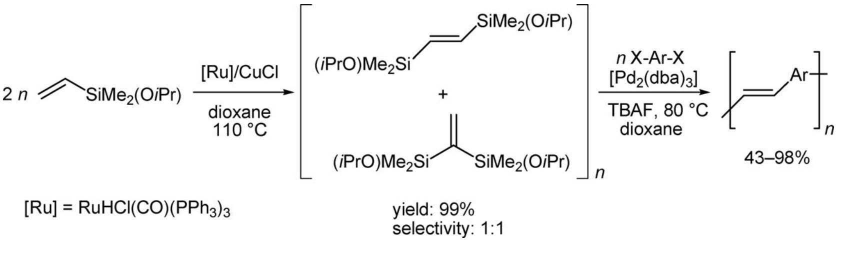


Scheme 13. Synthesis of poly(arylenevinylene)s.

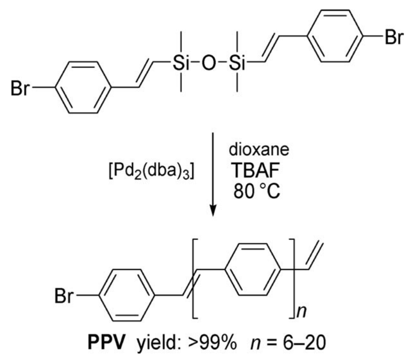
Another approach to the one-pot synthesis of PAVs is successive silylative coupling and Hiyama coupling proceeding via (*E*)-1,2-bis(silyl)ethene intermediates. The silylative coupling of isopropoxydimethylvinylsilane (Scheme 14) proceeded successfully in the presence of [$RuHCl(CO)(PPh_3)_3$] (2 mol-%) in dioxane, and the starting vinylsilane was efficiently transformed into an almost equimolar mixture of the isomeric (*E*)-1,2-bis(isopropoxy-dimethylsilyl)ethene and 1,1-bis(isopropoxydimethylsilyl)ethene. Next, palladium-catalysed coupling of these isomeric bis(silyl)ethenes with aryl dihalides in the presence of TBAF and $Pd_2(dba)_3$ catalyst proceeded stereoselectively to give satisfactory yields of the desired poly(arylenevinylene)s (Scheme 14).[18]

This is a new, efficient and highly stereoselective one-pot synthetic methodology for the construction of (*E*)-poly(arylenevinylene)s based on palladium-catalysed Hiyama cross-coupling of cyclic bis(silyl)ethenes or sequential silylative coupling and Hiyama cross-coupling of isopropoxydimethylvinylsilane with aryl dihalides.

1,3-Bis[(*E*)-4-bromostyryl]disiloxane (Scheme 15) also undergoes desilylative homocoupling at 80 °C to afford poly(phenylene-vinylene) derivatives with high yields (>99%) and stereoselectivities (>99% *E*).[27]



Scheme 14. One-pot synthesis of poly(arylenevinylene)s.



Scheme 15. Synthesis of poly(arylenevinylene)s from 1,3-bis[(*E*)-4-bromostyryl]disiloxane.

Silylative Coupling in the Synthesis of Styryl Halides and Styryl Ethers

The combination of ruthenium-catalysed silylative coupling (in both inter- and intramolecular fashion) with electrophilic halodesilylation has been used for the stereoselective preparation of synthetically useful alkenyl halides or dihalides.[30]

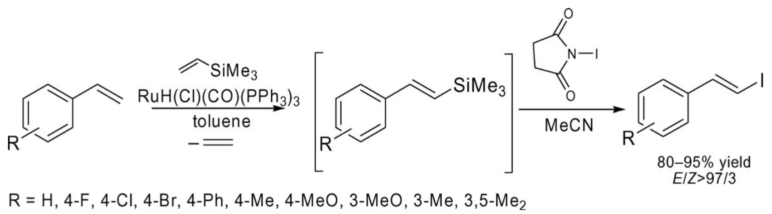
$RuH(Cl)(CO)(PPh_3)_3$-catalysed (*E*)-selective silylative coupling of styrenes with trimethylvinylsilane and subsequent *N*-iodosuccinimide-mediated iododesilylation has been reported as a valuable synthetic method for the one-pot conversion of easily available and relative inexpensive styrenes into (*E*)-β-arylvinyl iodides,[31] which are widely applied as extremely useful building blocks in transition-metal-catalysed organic transformations and natural products synthesis (Scheme 16).[31] Neither reaction is air-sensitive, and both can be performed with commercially available reagents and solvents without further purification. Under the optimal conditions, substituted styrenes bearing functional groups such as –Me, –Ph, –OMe, –Cl, –Br and –F reacted successfully to give the (*E*)-β-arylvinyl iodides in high yields via the corresponding (*E*)-styrylsilane intermediates, irrespective of the substituents' electronic characters or positions on the aromatic ring.[31] Because alkyl-substituted vinylsilanes appear to be inactive in ruthenium-catalysed cross-metathesis, silylative coupling offers an attractive alternative to the selective synthesis of (*E*)-β-arylvinyl iodides.

The application of the ruthenium-catalysed one-pot silylative coupling/*N*-bromosuccinimide-mediated bromo-desilylation strategy to the synthesis of (*E*)-β-arylvinyl bromides has also been reported (Scheme 17). By this procedure, (*E*)-β-arylvinyl bromides were prepared from styrenes containing both electron-donating and electron-withdrawing groups with over 98% *E* selectivities and in high yields.[31]

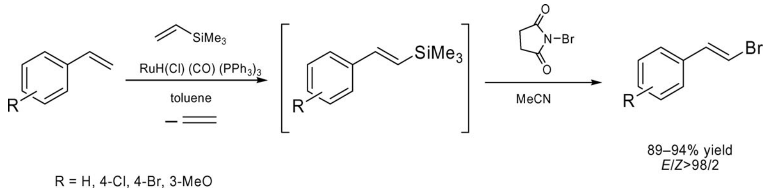
Because the presented methods avoid the use of large quantities of harmful metals or highly reactive organometallic compounds they provide an attractive alternative to the traditional synthetic routes employing alkynes or aldehydes as starting materials for the synthesis of (*E*)-arylvinyl halides.

The unique feature of the silylative coupling reaction, distinguishing this reaction from cross-metathesis, is the formation of 1,1-bis(silyl)ethene fragments under the given conditions. Although 1,1-bis(silyl)ethenes cannot be selectively obtained through direct silylative coupling (disproportionation) of vinylsilanes, new and efficient protocols for their synthesis through ruthenium-catalysed silylative coupling *exo*-cyclization of divinyl-substituted monomers and subsequent treatment with Grignard reagents or alcohols have been reported.[17,32] The resulting 1,1-bis(silyl)ethenes have been efficiently coupled with aryl iodides in the presence of silver nitrate and palladium acetate to give the corresponding 1,1-bis(silyl)-2-arylethenes in high yields. Two complementary three-step approaches based on sequential procedures involving one-pot silylative coupling cyclization/Grignard reagent treatment – Heck coupling[33a] or silylative coupling cyclization – Heck coupling/Grignard reaction[33b] have been reported.

Double bromodesilylation of the resulting 1,1-bis(trimethylsilyl)-2-arylethenes with excess *N*-bromosuccinimide (NBS) led to the formation of 1,1-dibromo-2-arylethenes

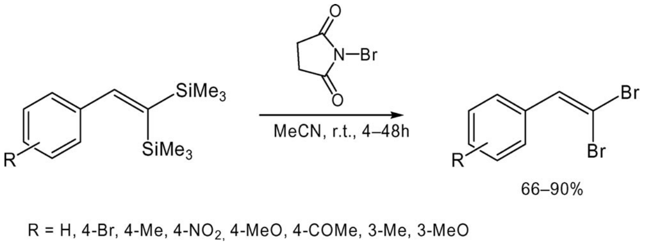


Scheme 16. Synthesis of (*E*)-β-arylvinyl iodides.



Scheme 17. Synthesis of (*E*)-β-arylvinyl bromides.

(Scheme 18),[34] which are valuable tools in the synthesis of di- and trisubstituted alkenes of defined stereochemistry such as triarylethenes, 2-aryl-1,1-dialkynylethenes, (*E*)-3-methyl-3-en-1-ynes, (*E*)- and (*Z*)-β-bromostyrenes, (*Z*)-1-aryl-1-bromoalk-1-enes and (*Z*)-2-bromobuta-1,3-dienes, as well as a wide range of alkyne derivatives (1-bromoalk-1-ynes, terminal and internal alkynes, 1,3-diynes).[35]

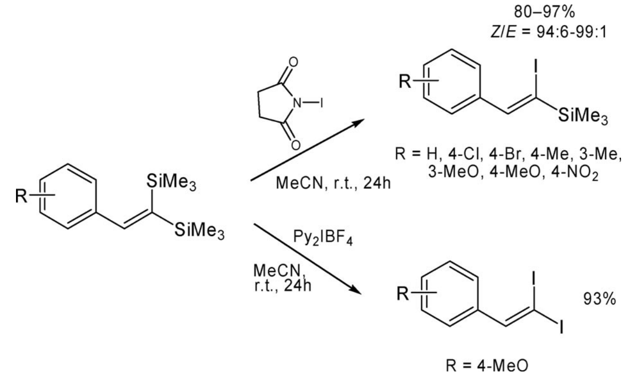


Scheme 18. Synthesis of 1,1-dibromo-2-arylethenes.

Mild conditions, good functional group compatibility and the simplicity of the experimental technique for this new approach to 1,1-dibromo-2-arylethenes are favourable features of this reaction.[34]

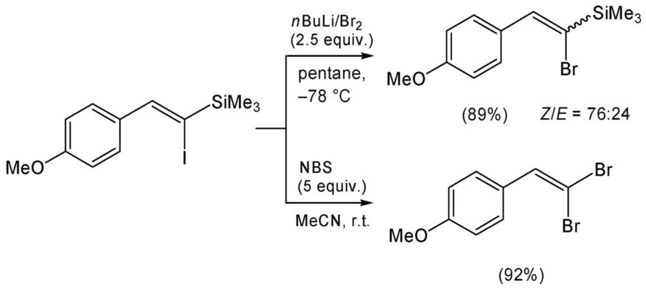
Iododesilylation of 1,1-bis(trimethylsilyl)-2-arylethenes in the presence of *N*-iodosuccinimide (NIS) or bis(pyridine)iodonium tetrafluoroborate exclusively afforded the monoiododesilylation products – (*Z*)-1-iodo-1-trimethylsilyl-2-arylethenes – as single stereoisomers (Scheme 19).[36] Stereodefined α-iodovinylsilanes can serve as precursors for the stereoselective preparation of 1-lithio-1-silylalkenes, trisubstituted olefins and secondary amides, as well as a variety of important organosilicon intermediates such as silyl-substituted alkenes, (*Z,E*)-1,3- and 1,4-dienes or α-bromovinylsilanes.[37] Despite the use of excesses of the iodinating agents in the iododesilylation processes (2 to 5 equiv. of NIS per silyl group), the reactions occurred selectively to give (*Z*)-α-iodovinylsilanes, with the exception of 1,1-bis(trimethylsilyl)-2-(4-methoxyphenyl)ethene, which in the presence of Py_2IBF_4 unexpectedly formed the doubly iodinated product – 1,1-diiodo-2-(4-methoxyphenyl)ethene – in 93% yield (Scheme 19).[36]

In contrast, the use of an *o*-substituted 1,1-bis(silyl)-2-arylethene – 1,1-bis(trimethylsilyl)-2-(2-methylphenyl)ethane – as a substrate under analogous conditions reversed the stereoselectivity, leading to the formation of (*E*)-1-iodo-1-trimethylsilyl-2-(2-methylphenyl)ethene as the predominant product.[36]



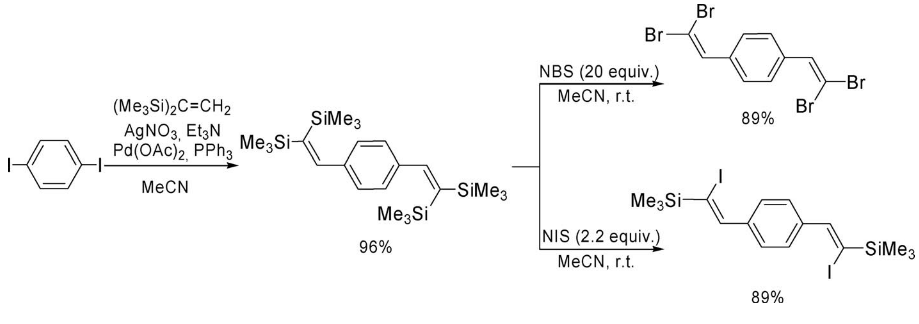
Scheme 19. Iododesilylation of 2-aryl-1,1-bis(trimethylsilyl)ethenes.

The treatment of (*Z*)-1-iodo-1-trimethylsilyl-2-arylethenes with *n*BuLi and molecular bromine at –78 °C led to selective substitution of iodine by bromine to afford 1-bromo-1-trimethylsilyl-2-arylethenes (Scheme 20). However, partial double bond isomerization occurred during this transformation to give a mixture of isomeric α-bromovinylsilanes.[36] On the other hand, quenching of the stereodefined (*Z*)-1-iodo-1-trimethylsilyl-2-arylethenes with excess *N*-bromosuccinimide afforded the 1,1-dibromo-2-arylethenes in good yields as a result of a simultaneous bromination/bromodesilylation process (Scheme 20).[36]

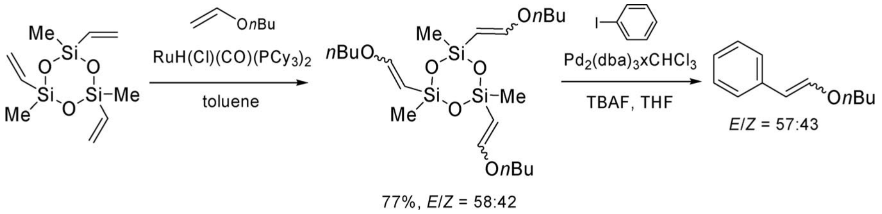


Scheme 20. Reactions of (*Z*)-1-iodo-1-trimethylsilyl-2-arylethenes with brominating agents.

An extension of this method to diiodoarenes has opened up a new attractive route for the synthesis of tetrasubstituted aromatic dienes. *N*-Halosuccinimide-mediated bromination or iodination of a tetrasilyl derivative of 1,4-divinylbenzene, easily obtained by Heck arylation of 1,1-bis(tri-



Scheme 21. Synthesis of halo-substituted divinylbenzenes.



Scheme 22. Synthesis of β-*n*-butoxystyrenes.

methylsilyl)ethene with 1,4-diiodobenzene, afforded 1,4-bis(2,2-dibromoethenyl)benzene and (*Z,Z*)-1,4-bis(2-iodo-2-trimethylsilylvinyl)benzene, respectively (Scheme 21).[34,36]

Silylative coupling of vinyl-substituted cyclosiloxanes with alkyl vinyl ethers, followed by desilylative arylation (Hiyama coupling), has been successfully applied to the synthesis of alkyl styryl ethers.[38] Sequential silylative coupling of trivinylcyclotrisiloxane with vinyl *n*-butyl ether and palladium-catalysed Hiyama coupling of the resulting β-*n*-butoxyvinyl-substituted cyclotrisiloxane with iodobenzene regioselectively produces a mixture of β-*n*-butoxystyrenes difficult to synthesize by other methods (Scheme 22).[39] It is worth noting that in contrast to the Pd-catalysed Heck arylation of alkyl vinyl ethers, no α-substituted product was formed under these conditions.[38]

Conclusions

Silylative couplings of olefins with vinyl-substituted silanes and siloxanes [in particular, cyclic 1,1-bis(silyl)ethene, vinyltriethoxysilane, vinyltrimethylsilane, divinyltetramethyldisiloxane and tetravinylcyclotetrasiloxane] appear to be valuable steps for subsequent desilylation reactions (i.e., Hiyama cross-coupling and halodesilylation) to provide highly π-conjugated systems. The methodology presented can be used not only for the synthesis of simple arylvinyl derivatives such as stilbenes, styryl halides and styryl ethers, but also for the preparation of complex multi-styryl-substituted arene derivatives, as well as arylene-vinylene polymers.

Thanks to the compatibility of the silylative couplings with sequential desilylation reactions, this useful and universal process is applicable as a direct method for alkene functionalization without any need for isolation of alkenylsilane intermediates, which is of great importance in organic synthesis.

The unique feature of this methodology is that the stereochemistry of this process can be controlled during the initial step because the subsequent desilylative arylation or halogenation proceed with retention of the configuration at the carbon atom and allow the formation of stereodefined products (Scheme 23).

Acknowledgments

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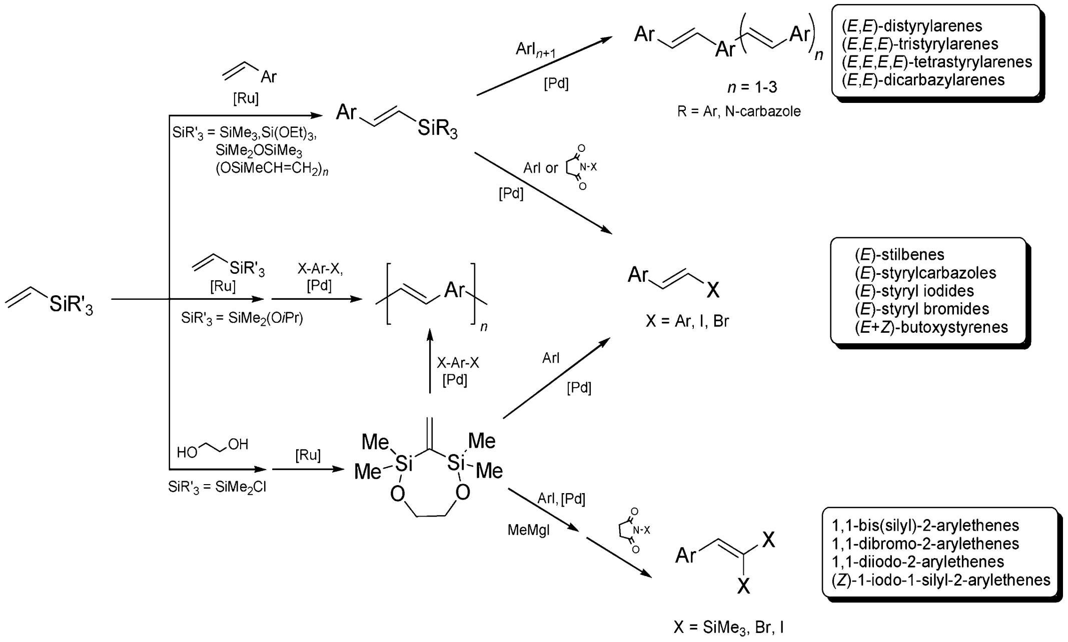

Scheme 23. Application of silylative coupling in the synthesis of arylvinyl derivatives.

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