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Highly Stereoselective Synthesis, Structure, and Application of (*E*)-9-[2-(Silyl)ethenyl]-9*H*-carbazoles

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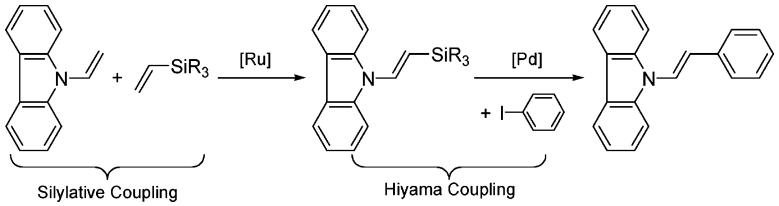

(*E*)-*N*-(Silyl)vinylcarbazole has been easily prepared via a new catalytic route, silylative coupling (**SC**) of vinylcarbazole with vinyltrisubstituted silanes catalyzed by $[RuH(Cl)(CO)(PCy_3)_2]$. X-ray structures of two silylvinylcarbazoles as first *N*-vinylcarbazole derivatives have been resolved. The Pd-catalyzed Hiyama coupling reaction (also as the tandem reaction with **SC**) of synthesized (*E*)-*N*-(triethoxysilyl)vinylcarbazole with iodobenzene has been performed to afford (*E*)-*N*-(phenylvinyl)-carbazole with high yield and stereoselectivity.

Introduction

Alkenylsilanes, particularly vinyl- and allylsilanes, make up a class of organosilicon compounds commonly used in organic synthesis by providing suitable regio- and stereoselective routes.[1] The lack of toxicity, high chemical stabilities, and low molecular weight of organosilanes make them ideal compounds for palladium-catalyzed cross-coupling with organic halides and pseudohalides.[2] In particular, Hiyama et al. have shown that organosilanes could be activated by a nucleophilic promotor.[3] Vinylsilanes can be efficiently prepared by several stereo- and regioselective methodologies involving classical stoichiometric routes from organometallic reagents and, more recently, transition-metal-catalyzed transformations of alkynes and silylalkynes (via the hydrosilylation), alkenes (the dehydrogenative silylation), and other silicon derivatives (for a review, see ref 4).

In the past 2 decades we developed two universal methods for the synthesis of well-defined molecular compounds with vinylsilicon functionality. Both methods, i.e., silylative coupling (also called *trans*-silylation or silyl group transfer) and *cross*-metathesis, are based on catalytic transformations of vinyl-silicon compounds with olefins and lead to the synthesis of the respective functionalized vinyl-silicon reagents (for a review, see ref 5). Whereas the *cross*-metathesis (**CM**) is catalyzed by well-defined Ru and Mo carbene complexes, the silylative coupling (**SC**) takes place in the presence of complexes initiating or generating [M]-H and [M]-Si bonds (where M = Ru, Rh, Ir) via the cleavage of the =C−H bond of the alkene and =C−Si bond of the vinylsilane, in contrast to *cross*-metathesis, which uses the same substrates and ends up with the same products (except the *gem*-isomer) through cleavage of the C=C bonds.

The mechanism of **SC** proved by Wakatsuki et al. and by us proceeds via insertion of vinylsilanes into the [M]-H

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(1) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. (b) Oshima, K. In *Science of Synthesis*; Fleming, I., Ed.; G. Thieme: Stuttgart, 2002; Vol.2, p 685. (c) *The Chemistry of Organosilicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: Chichester, 1998; Chapter 3.

(2) Denmark S. E.; Ober M. H. *Aldrichimica Acta* **2003**, *36*, 75−85.

(3) (a) Hiyama, T. *J. Organomet. Chem.* **2002**, *653*, 58. (b) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471. (c) Hiyama, T. In *Metal-catalyzed, Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Chapter 10.

(4) Marciniec, B.; Zaidlewicz, M.; Pietraszuk, C.; Kownacki, I. In *Comprehensive Organic Functional Group Transformations II*; Katritzky, A. R., Taylor, R. J. K., Eds.; Elsevier Science: Amsterdam, 2005; Charter 2.18.

(5) (a) Marciniec, B.; Pietraszuk, C. *Curr. Org. Chem.* **2003**, *7*, 691−735. (b) Marciniec, B.; Pietraszuk, C. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Wenheim, 2003; Vol. 2, Chapter 13. (c) Marciniec, B.; Pietraszuk, C. In *Topics in Organometallic Chemistry*; Bruneau, C., Dixneuf, P. H., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 2004; pp 197−248.

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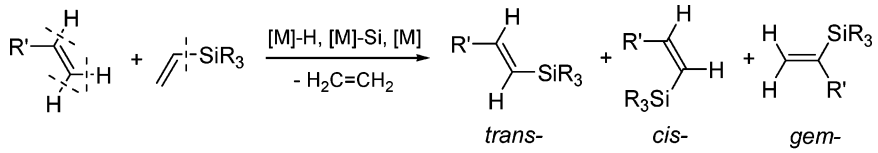
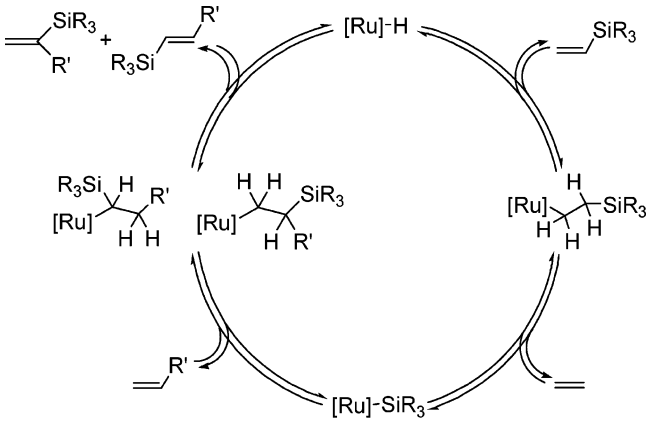
SCHEME 1



where: [M] = Ru, Rh, Ir and R' = SiR_3, OR, OCOR, alkyl, phenyl, 2-pyrrolidone,

SCHEME 2. Silylative Coupling Reaction Mechanism



where: R' = alkyl, phenyl, SiR_3; [Ru] = $Ru(Cl)(CO)(PPh_3)_2$

bond and β-Si transfer to the metal with elimination of ethylene to generate [M]-Si species, followed by insertion of alkene into [M]-Si and β-H transfer to the metal with elimination of the substituted vinylsilane.

Recently we have shown that complexes containing ruthenium-hydride [Ru-H] bond catalyze stereo- and/or regioselectively the *trans*-silylation of vinylsilanes with vinyl alkyl ethers,[7a] vinyl amides,[7b] and vinyl boronates[7c] to give (*E* + *Z*)- and (*E*)-*N*-2-(silyl)vinylamides and 1-silyl-1-(boryl)ethenes, respectively, which are difficult to prepare via other TM-catalyzed reactions such as *cross*-metathesis. The functionalization of cyclosiloxanes and cyclosilazanes[7d] as well as silsesquioxane[7e] is the next application of this new synthetic route, and very recently, alkyl-, aryl-, and alkenyl-substituted 1,1-bis(silyl)ethenes can be available by *exo*-cyclization of 1,2-bis(dimethylvinylsiloxy)ethane[7f] and *N,N′*-dimethyl,*N,N′*-bis(dimethylvinylsilyl)ethane-1,2-diamine[7g] followed by treatment with Grignard reagent and different alcohols, respectively.

In this paper we report the effective stereoselective silylative coupling of vinylcarbazole (as a first example of vinylamine) with vinyltrisubstituted silanes in the presence of $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**)[7h] in comparison with the catalytic activity of Grubbs' catalysts $[RuCl_2(=CHPh)(PCy_3)_2]$ (**II**) and $[RuCl_2(PCy_3)(IMesH_2)(=CHPh)]$ (**III**). The (*E*)-*N*-(silyl)vinylcarbazoles synthesized also undergo the effective Hiyama coupling reaction with iodobenzene to yield (*E*)-9-[2-(phenyl)ethenyl]-9-*H*-carbazole. A highly effective tandem reaction of silylative coupling−Hiyama coupling is a final target of this research.

Results and Discussion

The coupling reaction of the vinylsilanes with the general formula $H_2C{=}CH\text{-}SiR_3$ (where: SiR_3 = $SiMe_3$, $SiMe_2Ph$, $Si(OEt)_3$) with 9-vinylcarbazole catalyzed by ruthenium complex gave rise to evolution of ethylene and formation of suitable silyl-carbazole derivatives, according to Scheme 3.

The application of this catalytic system for silylative *cross*-coupling gives exclusively [(*E*)-2-(silyl)-1-(carbazol)]-ethene containing a *trans*-vinylene bond between silicon and nitrogen atoms. This kind of isomer was detected by ^1H NMR spectroscopy. $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**) (the most effective) was tested in the silylative *cross*-coupling process. The basic assumption of the synthetic procedure requires the absence of homocoupling products. Catalytic data are presented in Table 1.

The reaction was examined in an open system under a gentle stream of argon. However, when vinyltrimethylsilane was used, the reaction was conducted in a closed system because of the low boiling point (55 °C). The reaction was effectively catalyzed by **I** in toluene and *E*-(silyl)(carbazol)ethene was isolated successfully as a main product. The equimolar reaction of vinylsilanes with vinylcarbazole yields some bis(silyl)ethenes as byproducts. Since vinylcarbazole is inactive in **SC**, it can be used in excess to minimize the homocoupling of vinylsilane (see Table 1). Thus, under optimal conditions the catalyst (**I**) appeared to be the most efficient and particularly highly stereoselective for formation of *E*-products (accompanied by traces of homocoupling product).

In contrast to the ruthenium-hydride complex (catalyst **I**) the first generation Grubbs catalyst (**II**) is completely inactive in this reaction, but the second generation Grubbs catalyst (**III**) is effective, giving product with 35% yield (conversion of vinylsilane). The catalytic results provide the basis for the synthesis of silyl-derivatives of 9-carbazole. All *E*-products were isolated and characterized by standard NMR spectroscopy methods (see Experimental Section).

The structures of (*E*)-9-[2-(trimethylsilyl)ethenyl]-9*H*-carbazole (**1**) and (*E*)-9-[2-(dimethylphenylsilyl)ethenyl]-9*H*-carbazole (**2**) were characterized by X-ray crystallography (Figures 1 and 2).

The perspective views of molecules **1** and **2** are shown in Figures 1 and 2, respectively. Relevant geometric

(6) (a) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto; Y. *J. Chem. Soc., Chem. Commun*. **1991**, 703−704. (b) Marciniec, B.; Pietraszuk; C. *J. Chem. Soc., Chem. Commun*. **1995**, 2003−2004. (c) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320−4326.

(7) (a) Marciniec, B.; Kujawa, M.; Pietraszuk, C. *Organometallics* **2000**, *19*, 1677−1681. (b) Marciniec, B.; Chadyniak, D.; Krompiec, S. *Tetrahedron Lett*. **2004**, *45*, 4065−4068. (c) Jankowska, M.; Marciniec, B.; Pietraszuk, C.; Cytarska, J.; Zaidlewicz, M. *Tetrahedron Lett*. **2004**, *45*, 6615−6618. (d) Itami, Y.; Marciniec, B.; Kubicki, M. *Organometallics*, **2003**, *22*, 3717−3722. (e) Itami, Y.; Marciniec, B.; Kubicki, M. *Chem. Eur. J*. **2004**, *10*, 1239−1248. (f) Pawluc, P.; Marciniec, B.; Hreczycho, G.; Gaczewska, B.; Itami, Y. *J. Org. Chem*. **2005**, *70*, 370−372. (g) Pawluc, P.; Hreczycho, G.; Marciniec, B. *Synlett* **2005**, *7*, 1105−1108. (h) Marciniec, B.; Majchrzak, M.; Prukała, W.; Chadyniak, D. Polish Patent P-368097, 2004.

SCHEME 3. *trans*-Silylation Reaction via Cross-Coupling of 9-Vinylcarbazole with Various Vinylsilanes

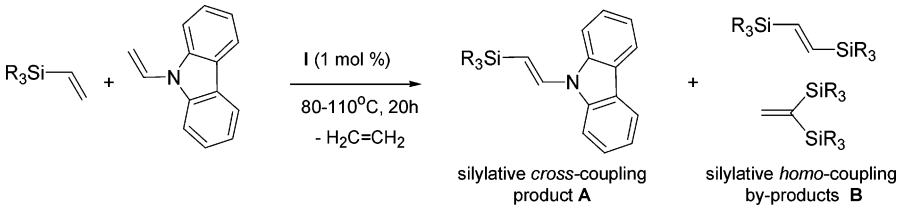


TABLE 1. Results of Silylative Coupling Reaction of Vinyltrisubstituted Silanes with 9-vinylcarbazole Catalyzed by I, II and III Ruthenium Catalysts

molar ratio ViSi/ViN	catalyst	conv of vinylsilane (%)	selectivity (%) product *cross*-A	selectivity (%) products *homo*-B	polymerization products [f]
		H_2C=CH−$SiMe_3$ [a]			
1:1	**I**	90[c]	80	20	trace
1:2	**I**	>99[c]	>99		trace
		H_2C=CH−$SiMe_2Ph$ [b]			
1:1	**I**	94[c]; 97[d]	>99	trace (*trans*)	trace
1:2	**I**	>99[c]	>99		middle
		>99[d]	>99		trace
		H_2C=CH−$Si(OEt)_3$ [b]			
1:1	**I**	82[c]	90	10	trace
1:2	**I**	>99[c]	93	7	trace
		>97[d]	95	4	trace
1:3	**I**	>99[c]	90	10	middle
		>99[d]	95	5	trace
3:1	**II**	0[e]	0		
	III	35[e]	>99		trace

[a] Reaction conditions: [Ru]:[ViSi] = 0.1:1; t = 20 h; T = 80−85 °C; Ar (closed system); toluene. [b] Reaction conditions: [Ru]:[ViSi] = 0.1:1; t = 20 h; T = 105−110 °C; Ar (open system); toluene. [c] 1 M. [d] 0.5 M. [e] [Ru=CHPh]:[ViSi]:[ViN] = 0.05:3:1; t = 20 h; T = 40°C; Ar (open system); CH_2Cl_2 0.5 M. [f] Uncontrolled radical polymerization of vinylcarbazole.

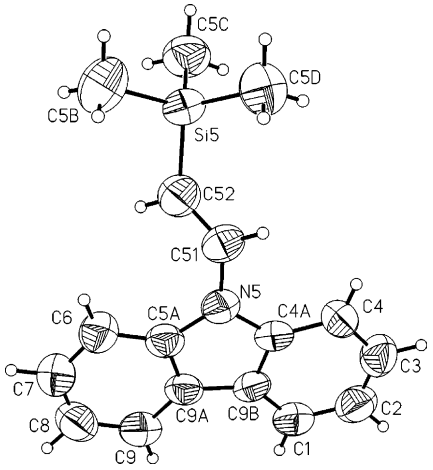


FIGURE 1. Thermal-ellipsoid representation of the compound **1**.[10] The ellipsoids are drawn at a 33% probability level, and hydrogen atoms are depicted as radii of arbitrary values.

parameters are compared in Table 2. In both compounds the bond lengths and angles are similar and close to typical values; however, to our surprise it turned out that there is only one structure of a *N*-vinylcarbazole derivative in the Cambridge Crystallographic Database,[8] called *N*-vinylcarbazole.[9]

The carbazole ring systems are almost perfectly planar, with maximum deviations of 0.015(5) Å for **1** and 0.016-

TABLE 2. Crystal and Structure Refinement Data for Compounds 1 and 2

	1	**2**
formula	$C_{17}H_{19}NSi$	$C_{22}H_{21}NSi$
M_r	265.42	327.49
crystal system	monoclinic	triclinic
space group	$P2_1/n$	P-1
cell dimensions:		
a (Å)	14.789(3)	8.7723(18)
b (Å)	6.036(1)	8.8405(8)
c (Å)	18.275(4)	11.9797(11)
α (deg)	90	81.375(8)
β (deg)	106.03(3)	78.537(13)
γ (deg)	90	85.571(13)
V (Å^3)	1567.9(5)	899.1(2)
Z	4	2
d_{calc} (g cm^{-3})	1.12	1.21
μ (mm^{-1})	1.19	1.14
crystal size (mm)	0.3, 0.08, 0.05	0.2, 0.2, 0.1
$2\theta_{max}$	120	150
independent reflections	1683	3524
R[F, $I > 2\sigma(I)$]	0.0583	0.0448
wR [F^2, all data]	0.1229	0.0922
S	0.981	1.041
$\Delta\rho_{max}/\Delta\rho_{min}$	0.19/−0.25	0.33/−0.31

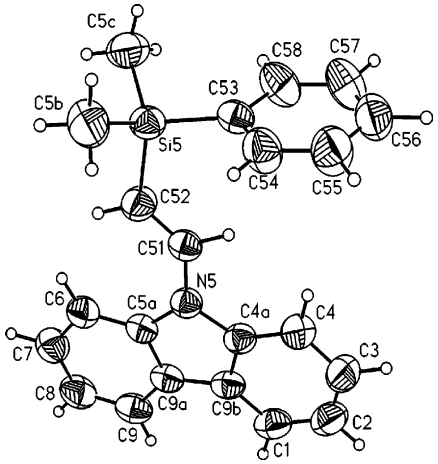
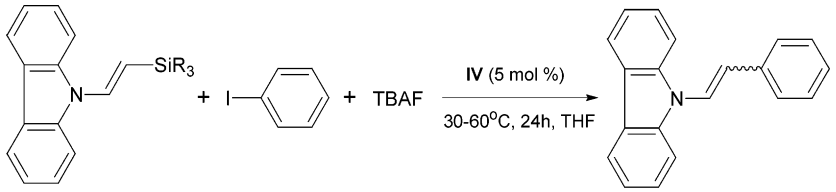


FIGURE 2. Thermal-ellipsoid representation of the compound **2**.[10] The ellipsoids are drawn at a 50% probability level, and hydrogen atoms are depicted as radii of arbitrary values.

(2) Å for **2**. This planarity is also confirmed by small values of dihedral angels between the least-squares planes of thermal six-membered rings: 1.0(3)° and 0.49-(13)° for **1** and **2**, respectively. In **2** the carbon atoms of the vinyl group and the silicon atom do not deviate much from the carbazole plane, whereas in **1** these deviations are large (cf. torsion angles, see Table 3). The plane of

(8) Allen, F. H. *Acta Crystalogr. Part B,* **2002**, *58*, 380.
(9) Tsutsui, K.; Hirotsu, K.; Umesaki, M.; Kurahashi, M.; Shimada, A.; Higuchi, T. *Acta Crystalogr., Sect. B* **1976**, *32*, 3049.

SCHEME 4. Hiyama Coupling Reaction of (*E*)-9-[2-(Silyl)ethenyl]-9*H*-carbazole (1, 2, 3) with Iodobenzene



where: SiR_3 = $SiMe_3$ (**1**), $SiMe_2Ph$ (**2**), $Si(OEt)_3$ (**3**),

SCHEME 5. Tandem Reaction: Silylative Coupling of 9-Vinylcarbazole with Vinyltriethoxysilane and Hiyama Coupling Reaction of (*E*)-9-[2-(Triethoxysilyl)ethenyl]-9*H*-carbazole (3) with Iodobenzene

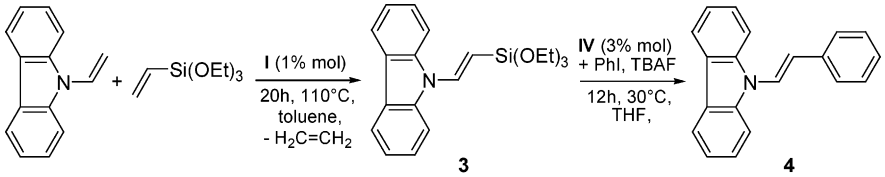


TABLE 3. Selected Bond Distances (Å), Bond Angles (deg), and Torsions Angle (deg) for Compounds 1 and 2 with su's in Parentheses

	1	2
C4A−N5	1.417(6)	1.404(2)
N5−C5A	1.412(6)	1.402(2)
N5−C51	1.383(7)	1.400(2)
C51−C52	1.306(6)	1.306(3)
C52−Si5	1.852(6)	1.860(2)
Si5−C5B	1.868(6)	1.858(3)
Si5−C5C	1.848(5)	1.862(3)
Si5−C5D	1.853(5)	
Si5−C53		1.873(2)
C9A−C9B	1.442(6)	1.437(3)
C4A−N5−C5A	106.4(5)	108.28(14)
C4A−N5−C51	123.2(4)	121.84(15)
C5A−N5−C51	127.9(4)	129.54(16)
N5−C51−C52	129.0(6)	130.75(19)
C51−C52−Si5	128.4(5)	123.11(17)
C4A−N5−C51−C52	139.3(6)	178.3(2)
N5−C51−C52−Si5	-178.0(4)	-179.28(15)

TABLE 4. Results of Catalytic Transformation of Silyl-carbazole Derivatives with Iodobenzene via the Hiyama Coupling Reaction Catalyzed by IV[a]

SiR_3	temp (°C)	conv of iodobenzene (%)	selectivity (%) *E*	selectivity (%) *Z*	yield (%)
$SiMe_3$	40	12	80	20	11
	60[b]	54	65	35	50
$SiMe_2Ph$	40	7	95	5	7
	60[c]	76	60	40	36
$Si(OEt)_3$	30	95	99	1	95
	40[b]	99	95	5	94
	60[b]	99	70	30	90

[a] Reaction conditions: $[Pd_2(dba)_3]$:[PhI]:[Si]:[TBAF] = 0.05:0.9:1:1.1; T = 30−60 °C; Ar (open system); THF 0.5 M. t = 24 h. [b,c] Higher temperature of reaction results in higher amount of biphenyl (*b*, 2−5%; *c*, 30%) and some amount of carbazole.

the phenyl ring in **2** is almost perpendicular to the carbazole plane (dihedral angle is 87.87(6)°).

The next step of the research was the application of trisubstituted-silyl derivatives of vinylene-carbazole (**1**, **2**, and **3**) in the Hiyama coupling reaction to obtain organic compounds containing a nitrogen atom characterized by high π-conjugation system bonds. The Hiyama coupling of the silyl-vinylcarbazole with iodobenzene was performed in the presence of a $[Pd_2(dba)_3]$/TBAF system in THF to convert it stereoselectively to (*E*)-9-[2-(phenyl)-ethenyl]-9*H*-carbazole as Scheme 4 depicts.

The results of catalytic screening are collected in Table 4. To determine the rate and selectivity of this process, silanes with different substituents at the silicon atom were used. The results of catalytic tests show unambiguously that the most suitable silyl-carbazole derivative substrate is compound **3** (containing ethoxyl as electron-withdrawing groups). The reason is that this compound makes it possible to obtain compound **4** with high efficiency and selectivity in mild temperature conditions. For the derivatives with $SiMe_3$ and $SiMe_2Ph$ groups, the Hiyama coupling at 30 °C occurs with a very low final yield. When the temperature of the reaction was raised up to 40 and 60 °C, an increase in the amount of *Z*-isomer was observed in the reaction mixture. Moreover, when compound **2** is used in the reaction, the desilylation, i.e., the Si-C sp^2 bond cleavage occurs probably simultaneously at two sites: in the silylene-vinylene fragment =CH−Si− and the silylene-phenylene fragment −Si−C_6H_5. It is supported by the large amount of biphenyl obtained and thus a small final efficiency of the reaction.

On the basis of catalytic results, additional experiments were carried out on the tandem reaction system (without isolation of compound **3**), according to Scheme 5:

The first step (**SC**) was to synthesize "product-substrate" **3** in a minireactor. Conversion of substrates (>99%), selectivity (>99%), and yield of the process (95%) were determined using a GC method with internal standard. Then, a suitable amount of the reaction mixture was taken, the excess of toluene was evaporated, and components for the Hiyama reaction (catalyst **IV**, PhI, TBAF, and THF) were introduced. The second step was performed at lower temperature (30 °C) to avoid isomerization of product **4**. The results are collected in Table 5.

The results clearly show that the best catalytic system contains a small excess of **3** relative to iodobenzene. It allows iodobenzene to react with product-substrate **3** to

TABLE 5. Results of Catalytic Transformation of 3 with Iodobenzene via Hiyama Coupling Catalyzed by IV[a]

molar ratio PhI/ViSi	time (h)	conv of iodobenzene (%)	selectivity (%) E	selectivity (%) Z	cross-linking of byproducts
1:1.2[b]	16	70	>99	trace	middle (dense solution)
1:1.2	5	93	>99		
1:1.25[c]	12	91	>99	trace	trace

[a] Reaction conditions: $[Pd_2(dba)_3]$:[Si]:[TBAF] = 0.03:1:1.2; T = 30°C; Ar (open system); THF 0.6M. [b] $[Pd_2(dba)_3]$:[Si] = 0.02:1. [c] THF 0.25 M.

give product **4** without biphenyl formation. Moreover, the reduction of the catalyst amount to 2 mol % requires more solvent and longer reaction time (12 h). The above presented preliminary research results of the Hiyama reaction with the use of silyl derivative of carbazole are the subject of detailed study of its application to obtain new organic compounds via the tandem silylative coupling-Hiyama coupling methodology.

Conclusions

In this paper a new effective synthesis of (*E*)-9-[2-(silyl)ethenyl]-9*H*-carbazole has been demonstrated via a highly stereoselective silylative coupling reaction of vinylcarbazole with vinyltrisubstituted silanes catalyzed by $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**). The X-ray crystal structures of trimethylsilyl- (**1**) and dimethylphenylsilyl- (**2**) vinyl carbazoles as the first structural analysis of *N*-vinylcarbazole derivatives have been solved. The Hiyama coupling reaction of the synthesized (*E*)-9-[2-(triethoxysilyl)-ethenyl]-9*H*-carbazole (**1**) with iodobenzene gives (*E*)-9-[2-(phenyl)ethenyl]-9*H*-carbazole (**4**) with high stereoselectivity. Finally, a tandem silylative coupling−Hiyama coupling reaction performed under mild conditions makes it possible to obtain **4** with high efficiency.

Experimental Section

General Methods. ^1H NMR (300 MHz), ^{13}C NMR (75 MHz), ^{29}Si NMR (60 MHz), and DEPT spectra were recorded on a 300 MHz spectrometer in C_6D_6 (or CD_3COCD_3, $CDCl_3$) solution. Chemical shifts are reported in δ (ppm) with reference to the residue solvent (CH_3Cl) peak for ^1H and ^{13}C and to TMS for ^{29}Si. Analytical gas chromatographic (GC) analyses were performed on a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. Mass spectra of the monomers and products were obtained by GC−MS analysis (with a BD-5 capillary column (30 m) and an ion trap detector. High-resolution mass spectroscopic (HRMS) analyses were performed on a mass spectrometer. Thin-layer chromatography (TLC) was made on plates coated with 250 μm thick silica gel, and column chromatography was conducted with silica gel 60 (70−230 mesh). Benzene and hexane were dried by distillation from sodium hydride, similarly toluene and diethyl ether were distilled from sodium and hexane from calcium hydride under argon. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All reactions were carried out under dry argon atmosphere. Melting points are uncorrected and were determined by using a melting point apparatus.

Materials. The following chemicals were used: benzene, CH_2Cl_2, EtOAc, toluene, decane, dodecane, diethyl ether, tetrahydrofurane, hexane, iodobenzene, tetrabutylammonium fluoride (TBAF), 9-vinylcarbazole, vinyltrimethylsilane, vinyldimethylphenylsilane, vinyltriethoxysilane, C_6D_6, CD_3COCD_3, and Grubbs' catalysts, $[RuCl_2(PCy_3)_2(=CHPh)]$ (**II**) and $[RuCl_2(PCy_3)(IMesH_2)(=CHPh)]$ (**III**). The ruthenium and palladium complexes, $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**)[11a] and $[Pd_2(dba)_3]$ (**IV**),[11b] were prepared according to the literature procedure.

Catalytic Examinations of Silylative Coupling Reaction. In a typical catalytic test, the ruthenium catalyst **I** (1 mol %) was dissolved in a toluene and placed in a glass ampule under argon. Then the reagents and decane or dodecane as internal standard (5 vol % all components) were added (usually used at the molar ratio [Ru]:[ViSi]:[olefin] = 0.01:1:1(2 or 3)). After that, the ampule was heated at 105−110 °C for 20 h. In the catalytic test with vinyltrimethylsilane, the sealed glass ampule was heated at 80 °C for the same time.

Catalytic Examinations of Hiyama Coupling Reaction. In a typical catalytic test, the reagents and decane or dodecane as internal standard (5 vol % all components) were dissolved in a tetrahydrofurane and placed in a glass ampule under argon (usually used at the molar ratio [ViSi]:[PhJ]:[TBAF] = 1:0.9:1.1). Then the palladium catalyst **IV** (5 mol %) was added and the ampule was heated from 30 to 60 °C for 24 h.

Catalytic Examinations of Silylative Coupling and Hiyama Coupling. Tandem Reaction. In typical catalytic test the (*E*)-9-[2-(silyl)ethenyl)]-9*H*-carbazole is not isolated after silylative coupling reaction (amount calculated from GC analyses). Then, the next reagents and decane as internal standard (5 vol % all components) were dissolved in an appropriate amount of THF and placed in a glass ampule under argon (usually used in the molar ratio [ViSi]:[PhJ]:[TBAF] = 0.8:1:1.2). After that, the palladium catalyst **IV** (3 mol %) was added and the ampule was heated in 30 °C for 24 h.

During catalysis the conversion of the substrates was calculated using the internal standard method. The composition of the reaction mixture was analyzed by GC and GC−MS.

Syntheses of Silyl-carbazole Derivative Compounds. The syntheses were performed under argon using $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**) as the catalyst and dry, deoxygenated reagents and solvent. In all cases the final mixtures were isolated. The details are presented below.

(*E*)-9-[2-(Trimethylsilyl)ethenyl]-9*H*-carbazole (1). $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**) (49 mg, 0.068 mmol), toluene (6.82 mL), vinyltrimethylsilane (0.684 g, 6.82 mmol), and 9-vinylcarbazole (2.64 g, 13.64 mmol) were placed in a 15 mL glass ampule. The ampule was sealed and heated at 80 °C for 20 h. The final product was separated from residues of the catalyst and the remaining olefin using column with silica (hexane/EtOAc = 50:1, R_f = 0.65), to afford 1.09 g of **1** (4.11 mmol, 60% yield) as white and less-yellow crystals, mp 93.2−94.8 °C. ^1H NMR (C_6D_6, δ (ppm)): 0.19 (s, 9H, ($Si(CH_3)_3$), 5.93 (d, 1H, J_{H-H} = 17.1 Hz, -HC=C*H*-Si), 7.36 (t, 1H, Ph), 7.59 (t, 1H, Ph), 7.60 (d, 1H, Ph), 7.85 (d, 1H, J_{H-H} = 17.0 Hz, -HC=C*H*-N), 7.96 (d, 1H, Ph). ^{13}C NMR (C_6D_6, δ (ppm)): − 0.8, 111.2, 113.0, 120.6, 121.2, 124.8, 126.2, 133.5, 139.8. ^{29}Si NMR (C_6D_6, δ (ppm)): − 5.09. HRMS calcd for $C_{17}H_{19}NSi$: 265.12868, found 265.12999. Anal. Calcd for $C_{17}H_{19}NSi$: C 76.93, H 7.22, N 5.28. Found: C 76.64, H 7.20, N 5.26. Single crystals of **1** suitable for X-ray crystal structure were obtained by recrystallization from diethyl ether/hexane.

(*E*)-9-[2-(Dimethylphenylsilyl)ethenyl]-9*H*-carbazole (2). $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**) (49 mg, 0.068 mmol), toluene (6.82 mL), vinyldimethylphenylsilane (1.107 g, 6.82 mmol), and 9-vinylcarbazole (1.45 g, 7.50 mmol) were placed in a 20 mL glass minireactor. The mixture was heated at 105−110 °C for 20 h under an argon flow. After disappearance of the substrates was confirmed by GC analysis, the solvent was evaporated under vacuum and the final fraction was injected

(10) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.
(11) (a) Yi C. S.; Lee D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043. (b) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem*. **1974**, *65*, 253.

onto a silica gel column similarly to the synthesis of **1** (hexane/EtOAc = 50:1, R_f = 0.55), to afford 1.78 g of **2** (5.44 mmol, 80% yield) as white crystals, mp 96.5−98.0 °C (dec). ^{1}H NMR (C_6D_6, δ (ppm)): 0.46 (s, 6H, (Si(CH_3)$_2$), 6.06 (d, 1H, J_{H-H} = 17.3 Hz, Si-*H*C=CH-N), 7.21−7.98 (Ph), 7.28 (d, 1H, J_{H-H} = 17.3 Hz, -HC=C*H*-N). ^{13}C NMR (C_6D_6, δ (ppm)): −2.1, 110.3, 110.8, 120.2, 120.9, 124.2, 126.2, 127.9, 129.2, 133.9, 135.1, 139.3. ^{29}Si NMR (C_6D_6, δ (ppm)): − 8.88. HRMS calcd for $C_{22}H_{21}NSi$: 327.14433, found 327.14618. Anal. Calcd for $C_{22}H_{21}NSi$: C 80.68, H 6.46, N 4.28. Found: C 80.38, H 6.44, N 4.29. Single crystals of **2** suitable for X-ray crystal structure were obtained by recrystallization from diethyl ether/hexane.

***(E)*-9-[2-(Triethoxysilyl)ethenyl]-9*H*-carbazole (3).** [RuH(Cl)(CO)(PCy$_3$)$_2$] (**I**) (49 mg, 0.068 mmol), toluene (6.82 mL), vinyltriethoxysilane (1.298 g, 6.82 mmol), and 9-vinylcarbazole (2.64 g, 13.64 mmol) were placed in a 20 mL glass minireactor. The mixture was heated at 105−110 °C for 20 h under an argon flow. Then, the reaction mixture was distilled under reduced pressure (136−138 °C/1 mmHg), which afforded 1.47 g (4.14 mmol) of **3** in 65% as a colorless liquid. ^{1}H NMR (C_6D_6, δ (ppm)): 1.35 (t, 9H, CH_3), 3.98 (q, 6H, CH_2), 5.72 (d, 1H, J_{H-H} =17.3 Hz, Si-*H*C=CH-N), 7.33 (t, 1H, Ph), 7.50 (t, 1H, Ph), 7.77 (d, 1H, Ph), 7.78 (d, 1H, J_{H-H} =17.3 Hz, Si-HC=C*H*-N), 8.07 (d, 1H, Ph). ^{13}C NMR (C_6D_6, δ (ppm)): 18.5, 31.1, 111.2, 113.0, 120.5, 121.2, 124.8, 126.5, 134.1, 139.8. ^{29}Si NMR (C_6D_6, δ (ppm)): − 54.13. HRMS calcd for $C_{20}H_{25}NO_3Si$: 355.16037, found 355.16119. Anal. Calcd for $C_{20}H_{25}NO_3Si$: C 67.57, H 7.09, N 3.94. Found: C 67.69, H 7.11, N 3.93.

Syntheses of Carbazole-derivative Compound. The synthesis was performed under argon using [Pd$_2$(dba)$_3$] (**IV**) as the catalyst, reagents, and solvent. The final product was isolated from the reaction mixture. The details are presented below.

Synthesis of (*E*)-9-[2-(Phenyl)ethenyl]-9*H*-carbazole (4). [Pd$_2$(dba)$_3$] (**IV**) (1.37 mg, 0.0015 mmol), THF (0.2 mL), (*E*)-9-[-2-(triethoxysilyl)ethenyl]-9*H*-carbazole (35.4 mg, 0.1 mmol), tetrabutylammoniumfluoride (28.6 mg, 0.11 mmol), and iodobenzene (0.01 mL, 0.09 mmol) were placed in a 1.5 mL glass ampule. The mixture was heated at 30 °C for 24 h under an argon atmosphere. The degree of conversion was calculated by GC and GC−MS analyses. The final product was separated from the reaction mixture using column with silica (hexane/EtOAc = 30:1, R_f = 0.49), to afford 21.28 mg (79% yield) of **4** as white and less-yellow crystals, mp 116−120 °C (dec). ^{1}H NMR (C_6D_6, δ (ppm)): 6.77 (d, 1H, J_{H-H} = 14.3 Hz, >N−C*H*=), 7.25−7.17 (m, 7H, 3,6-H in carbazole and Ph), 7.29 (d, 1H, J_{H-H} = 14.5 Hz, Ph-C*H*=CH-N), 7.32 (t, 2H, J_{H-H} = 8.3 Hz, 2,7-H in carbazole), 7.42 (d, 2H, J_{H-H} = 8.2 Hz, 1,8-H in carbazole), 7.96 (d, 2H, J_{H-H} = 7.7 Hz, 4,5-H in carbazole). ^{13}C NMR (C_6D_6, δ (ppm)): 111.0, 120.5, 120.6, 121.1, 123.6, 124.6, 126.3, 126.5, 127.4, 129.0, 136.8, 140.0. HRMS calcd for $C_{20}H_{15}N$: 269.12045, found 269.12056.

X-ray Crystal Structure Analysis. X-ray data were collected at room temperature on a four-circle diffractometer[12] by the ω-2θ scan method, using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). All measured reflections were corrected for Lorentz and polarization effects.[13] The structures were solved using SHELXS97 program[13] and refined by full-matrix least squares on F^2 with SHELXL97.[14] All non-hydrogen atoms were refined anisotropically for **1** hydrogen atoms were placed geometrically, in idealized positions, and included in the refinement as the riding model with U_{iso} set at 1.2 times U_{eq} of the appropriate carrier atom (1.3 for methyl groups). For compound **2** all hydrogen atoms were located in subsequent difference Fourier maps and their positional as well as isotropic thermal parameters were freely refined. Other crystallographic data collection and refinement data are presented in Table 2.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, nos. CCDC 216010 for compound **1** and CCDC 216009 for compound **2**. Copies of the data may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44 (1223) 336−033, e-mail: deposit@ccdc.cam.ac.uk, or www: http://www.ccdc.cam.ac.uk.

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Supporting Information Available: X-ray crystallographic data for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JO051629T

(12) KUMA KM4 User's Guide, Version 5.0; KUMA Diffraction: Wroclaw, Poland, 1991.

(13) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen (Germany), 1997.

(14) *Sterechemical Workstation*; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1989.