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An efficient catalytic route for the synthesis of silane coupling agents based on 1,1,3,3-tetramethyldisiloxane core

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Abstract: We report studies concerning the selective mono-functionalization of 1,1,3,3-tetramethyldisiloxane (TMDSO) with vinyl-substituted silicon derivatives *via* the hydrosilylation reaction. Examinations of platinum- and rhodium-based catalysts in the reactions between TMDSO and exemplary vinyl-containing silicon derivatives have enabled appointing the most efficient catalyst, whose application leads to selective partial functionalization of the disiloxane reagent and simultaneous formation of only *β*-regioisomers.

Introduction

The transition metal-catalyzed addition of Si-H bond to carbon-carbon multiple bonds is a commonly used and efficient tool for the synthesis of a wide gamut of organosilanes or polysiloxanes as well as for cross-linking of silicone fluids,[1] including silylfunctionalization of unsaturated organic[2] or organosilicon[3] polymers for different applications, depending on the type and reactivity of the introduced functional groups. For instance, derivatives of 1,1,3,3-tetramethyldisiloxane (TMDSO) partially modified with (alkoxy)vinyl silanes ($(R^1O)_nR_{3-n}SiCH=CH_2$) are widely used as essential functionalizing agents of fluorinated polyethers,[4] acrylic or methacrylic esters[5] or polysiloxane ingredients for heat conductive silicone composition,[6] while the products of one-sided TMDSO functionalization with olefins or vinylsilanes with organic substituents at silicon atom ($R_3SiCH=CH_2$) are surfactants for production of skin-care cosmetics[7a,b] or coatings and printing ink compositions.[7c]

As indicated by the number of patents that have appeared over the bygone 20 years, particularly those concerning the synthesis and utilization of organic and oganosilicon polymers[2-7] equipped with reactive functional groups of various types, the interest in the synthesis of different multifunctional silicon hydrides for such purposes is growing.

Unsymmetrically substituted siloxanes, i.e. those having on the one side Si-H moiety, and on the opposite side a reactive or specific functional group, can be prepared by two routes, namely, by hydrolysis and co-condensation of appropriate monochlorosilanes (RMe_2SiCl and $HSiMe_2SiCl$)[8] or condensation of silanolates (RMe_2SiOLi) with $HSiMe_2Cl$[9] as well as through partial functionalization of 1,1,3,3-tetramethyldisiloxane (TMDSO) with various organic or organosilicon unsaturated reagents *via* hydrosilylation reaction. In view of literature data, the latter is the most convenient and common protocol used for obtaining derivatives of this type. The hydrosilylation reaction, in most cases catalyzed by transition metal complexes, in particular Pt (Karstedt's catalyst, H_2PtCl_6) and Rh (Wilkinson's catalyst, $[RhCl_3(t\text{-}Bu_2S)_3]$, allowed modification of TMDSO core, with the functional groups, such as PEG of different lengths,[10] 3-(alkyloxy)propyl,[11] organic epoxides,[12] 3-(benzophenoxy)-propyl,[13] 3-(methacryloxy)propyl,[14] 3-(amino)propyl,[15] aryloxy-alkyl or arylalkyl.[16]

The hydrosilylation protocol was successfully applied for partial functionalization of 1,1,3,3-tetramethyldisiloxane with silicon derivatives, however the number of the latter, which were reported as functionalizing reagents, is limited to a few examples of simple commercially available vinylsilanes such as $H_2C=CHSiR^1{}_n(OR^2)_{3-n}$,[17] $H_2C=CHSiMe_3$[4a,7a,b,18] and vinyl siloxanes[19] or allyl silane of the type $H_2C=CHCH_2Si(OEt)_3$.[20] As reported in the above-cited references, in the systems in which vinyl-substituted organic[12, 16] or organosilicon[4a,7a,b,17-19] compounds were used as reagents, the formation of *α*- and *β*-isomeric was observed, regardless of the platinum or rhodium based catalysts.

In view of the literature data briefly described above, in particular the broad scope of applications of TMDSO derivatives endowed on the one side with hydrolysable silicon functions, we decided to develop a catalytic system allowing an efficient synthesis of mono-functionalized 1,1,3,3-tetramethyldisiloxane derivatives *via* hydrosilylation as well as selective formation of β-addition products. This type of bifunctional compounds based on flexible disiloxane core, bearing in its structure two reactive moieties, i.e. SiH moiety, which can take part in hydrosilylation process, and a silicon functional group, susceptible towards hydrolysis and condensation, seem to be very interesting functionalizing agents (modifiers) of a wide range of vinyl containing molecular or macromolecular organosilicon materials as well as polyene macromolecules.[21]

Results and Discussion

Therefore, considering the above, our work presented in this paper was focused on the development of an efficient catalytic method of 1,1,3,3-tetramethyldisiloxane mono-functionalization *via* hydrosilylation process leading to the corresponding bifunctional organosilicon modifiers having in its structure simultaneously HSi≡ bond and other reactive groups.

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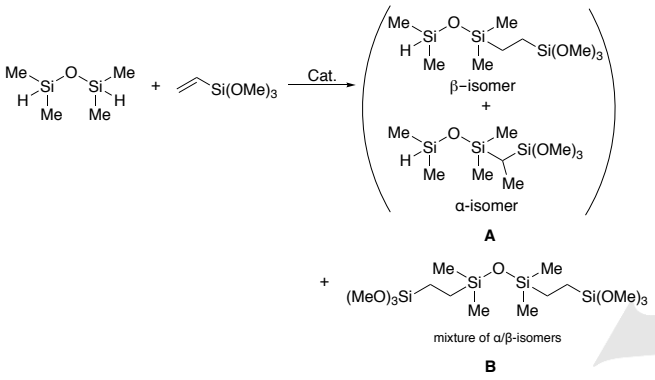
Therefore, in order to find the best conditions for efficient synthesis of mono-functionalized 1,1,3,3-tetramethyldisiloxane, the initial work was focused on optimization of hydrosilylation process. At the beginning, catalytic examinations were carried out in the model reaction of 1,1,3,3-tetramethyldisiloxane and vinyltrimetoxysilane at the equimolar ratio (Scheme 1) with employment of three homogeneous catalysts, namely Pt-Karstedt's complex (**C1**), the most active and commonly used in industrial processes based on hydrosilylation[1] and rhodium complexes [{Rh(μ-Cl)(COD)}$_2$][1] (**C2**) and [RhCl(PPh$_3$)$_3$][1] (**C3**) also known as efficient hydrosilylation catalysts as well as two heterogeneous metallic catalysts such as Pt/SDB (styrene-divinylbenzene *co*-polymer) (**C4**) and Rh/SDB (**C5**) for the sake of comparison.



Scheme 1. Products distribution on the model reaction.

The results summarized in Table 1, demonstrate that the homogeneous promoters **C1**-**C3** and exemplary platinum heterogeneous catalyst **C4** proved to be active in the studied model reaction and catalyzed efficiently the conversion of initial substrates to hydrosilylation products. However, irrespectively of the catalyst used, always monohydrosilylation derivative **A** was accompanied by bishydrosilylation product **B**, even at the mild reaction conditions (50 °C). Furthermore, in both types of hydrosilylation products the GCMS and ^{1}H NMR analyzes revealed the presence of *α* and *β* regioisomers. Nevertheless, comparing the results of hydrosilylation tests, conducted for all catalysts (see Table 1), the most advantageous ratio between products **A** (monohydrosilylation) and **B** (bishydrosilylation) was found in the *post*-reaction mixture obtained with the use of pre-catalyst **C2**. Additionally, in the presence of this complex the contribution of *α*-isomer in product **A** was also significantly smaller than for the other catalysts. Surprisingly, in view of our earlier experience,[22] **C4** proved to be less effective than the homogeneous TM-pre-catalysts and much less selective, as one would expect of this heterogeneous catalyst. (see Table 1). The analogous rhodium catalyst (**C5**) proved to be poorly effective in the studied model reaction giving both, low conversion of the initial silicon reagent and less than 5% yield of derivative **A**, which was additionally accompanied with TMDSO dehydrocoupling products such as 1,1,3,3,5,5,7,7-octamethyltetrasiloxane.

Furthermore, catalytic tests carried out with the use of most promising rhodium complex (**C2**) in the model reagents system (Scheme 1), in hexane as reaction environment, revealed only a moderate influence of reduced concentration of reagents on the increase in the reaction selectivity towards product **A** (see Table 1). Moreover, dilution of the reagents resulted in a significant decrease in the selectivity towards β-regioisomer, in comparison with the results obtained for the reaction in the solvent-free systems (see Table 1).

Table 1. Hydrosilylation of vinyltrimethoxysilane by 1,1,3,3 tetramethyldisiloxane in stoichiometric ratio.

Vinylsilane	Catalyst	Conversion of ViSiR$_3$ (%)[g]	Yield of products (%)		Product **A** regioselectivity (%)	
			A	**B**	**α**	**β**
1	**C1**[a]	100	73.0	27.0	30.7	69.3
	C2[b]	100	83.8	16.2	21.5	78.5
	C3[b]	99	81.7	18.3	29.2	70.8
	C4[c]	93	82.8	17.8	37.5	62.5
	C5[c]	19	4.7	0	29.4	70.6
	C2[d]	100	90.6	9.4	26.7	73.3
	C2[e]	100	90.7	9.3	30.3	69.7
	C2[f]	100	91.8	8.2	32.3	67.7

C1 = Pt-Karstedt; **C2** = [{Rh(μ-Cl)(COD)}$_2$]; **C3** = [RhCl(PPh$_3$)$_3$]; **C4** = Pt/SDB (1% Pt); **C5** = Rh/SDB (1% Rh). Reaction conditions: T=50 °C, t= 24 h [H$_2$C=CH-] : [HSi≡] = 1 : 2, [a] - [Pt] : [H$_2$C=CH-] = 2x10^{-5} : 1, [b] - [Rh] : [H$_2$C=CH-] = 2x10^{-4} : 1, [c] - [M] : [H$_2$C=CH-] = 10^{-3} : 1, [d] - [Rh] : [H$_2$C=CH-] = 2x10^{-4} : 1 concentration of reagents in hexane – 50%, [e] - [Rh] : [H$_2$C=CH-] = 2x10^{-4} : 1 concentration of reagents in hexane – 25%, [f] - [Rh] : [H$_2$C=CH-] = 2x10^{-4} : 1 concentration of reagents in hexane – 10%, [g]Conversion yield were determined by GC analysis and calculated on the basis of ViSiR$_3$, using the solvent peak as a standard.

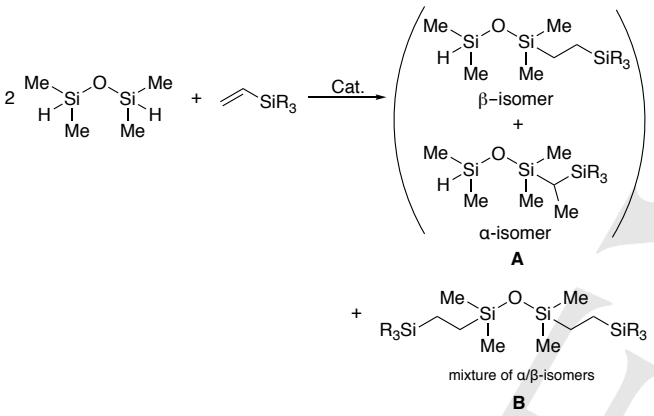
Therefore, it seemed obvious to us that the increase in the molar ratio of TMDSO to vinyl compound from 1 : 1 to 2 : 1, should have a significant impact on the products distribution in the reaction systems in which the molar ratio of HSi≡ bond to vinyl reagent formally is 4 : 1. Moreover, it is also expected that in some cases, particularly for more sterically hindered vinyl reagents, better distribution of *β/α*-regioisomers should be observed especially with predominance of mono-substituted *β*-isomeric products.

Therefore, at the subsequent step, the efficiency of **C1** - **C5** was examined in the model reaction, using this time 2 equivalents of TMDSO with respect to H$_2$C=CHSi(OMe)$_3$. The data obtained with the use of *in situ* IR technique, showed (see Table 2), that unlike the heterogeneous catalysts, the molecular ones operate quite rapidly under given conditions and they catalyzed the conversion of initial reagents to hydrosilylation products in a relatively short time. However, only with complex **C2**, the reaction proceeded towards the selective formation of the monohydrosilylation product **A**. The use of lower concentrations of catalyst **C1** ([Pt] : [H$_2$C=CH-] = 2x10^{-7} : 1) also gave good result in terms of selectivity towards partial hydrosilylation product (**A**), but unfortunately, it resulted in a deterioration of the ratio of regioisomers formed, i.e. in the

increased content of the α-addition product. Unfortunately, in the presence of the other homogeneous TM-complexes, i.e. **C1** and **C3** as well as the heterogeneous catalyst **C4**, the product **A** was always accompanied by the second derivative **B**. Similarly, as in the model reaction with the reagents at equimolar ratio (see Table 1), heterogeneous catalyst **C5** proved to be selective towards the formation of product **A**, but poorly active in this process giving this product with merely 7.8 % yield.

Therefore, taking into account the values of the selectivity and yield of product **A** formed in the presence of the studied catalysts (**C1**-**C5**), the most promising for further studies seemed to be catalysts **C1** and **C2**, because their use lead to the formation of the monohydrosilylation product **A** with high yield, and with predominance of *β*-isomer.

Thus, at subsequent steps the selected catalysts (**C1**, **C2**) were examined in the reactions of TMDSO with exemplary vinyl-functionalized silicon derivatives functionalized with silyl groups of different sizes, as shown in Scheme 2.



R_3 = $(OMe)_3$ (**1**); $(OEt)_3$ (**2**); $Me(OMe)_2$ (**3**); $(O^tBu)_3$ (**4**); $SiMe_2N(SiMe_3)_2$ (**5**); $(OEt)_2Ph$ (**6**); $(OEt)Ph_2$ (**7**)

Scheme 2. Products distribution in the reaction of TMDSO with selected vinylsilanes in the molar ratio 2 : 1.

The results summarized in Table 2 show that both homogeneous TM-precursors efficiently catalyze the addition of HSi≡ to the C-C double bond in the selected vinyl-substituted silicon reagents. , Nonetheless, in contrast to the Pt-Karstedt's catalyst (**C1**), the rhodium binuclear precursor **C2** proved to be significantly more selective towards the monohydrosilylation process, leading exclusively to the formation of product **A** for vinyl-silicon derivatives **2** – **5**, under the same reaction conditions. None of the complexes applied in hydrosilylation tested exhibited any differences in the formation of *α* and *β* regioisomers in the catalytic systems obtained on the basis of vinyl-functionalized silicon derivatives **2** and **3,** giving a mixture of isomers, of course, with predominance of *β*-product. Surprisingly, for the remaining vinyl-silicon compounds with significantly more sterically crowded structure, i.e. bearing in their structure bulky substituents at silicon (-O^tBu or – $SiMe_2N(SiMe_3)_2$ (compounds **4** and **5**), in the presence of both catalysts (**C1** and **C2**), the exclusive formation of *β* regioisomers was observed. However, unlike with the platinum promoter **C1**, the employment of the rhodium catalyst **C2** resulted in the selective formation of monohydrosilylation product **A**. As expected, employment of **C2** in the reactions of TMDSO with the vinylsilanes **6** and **7** bearing at silicon atom one or two phenyl rings, respectively, besides ethoxy substituents, resulted in selective formation of *β*-isomeric products. We did not expect that in the same reaction conditions that were applied for transformation of vinyl derivatives **2**–**5** to the corresponding products (see Table 2), the complete conversion of silanes 6 and **7** will require much more time, in comparison to that needed for vinyl derivatives 2-5, moreover it surprising that for compound **7** unexpected product **B** will be also observed. Moreover, when the higher molar ratio of TMDSO with respect to **7** was applied, e.g. 2.5 : 1, the formation of product **B** was not prevented, but instead, the undesired product of the siloxane dehydrocoupling process was detected. Therefore, it seems that in the studied reagent systems, the steric effects play a crucial role in the selective formation of *β*-regioisomeric products.

Generally, in the reaction systems containing an organosilicon reagent bearing in its structure two chemically equivalent Si-H bonds, as in TMDSO, formation of either partially functionalized or bisubstituted TMDSO derivatives takes place.

Table 2. Results of the reaction between TMDSO and vinyl-silicon derivative in the molar ratio 2 : 1.

SiR_3	Cat.	Conversion of $ViSiR_3$ (%)[d]	Time [h:min]	Yield of products (%)	Product **A** regioselectivity (%	
				A/B	**α**	**β**
	C1[a]	100.0	00:02	92.4/7.6 (93)	27.0	73.
	C1[b]	94.6	18:00	94.6/0	30.8	69.
1	**C2**[c]	100.0	00:42	100/0 (92)	18.8	81.
	C3[c]	98.8	02:21	96.2/3.8	23.3	76.
	C4[d]	92.7	24:00	96.0/4.0	26.6	73.
	C5[d]	22.0	24:00	7.8/0	26.5	73.
2	**C1**[a]	100.0	00:02	89.6/10.4	15.1	84.
	C2[c]	100.0	00:04	100/0 (98)	19.0	81.
3	**C1**[a]	100.0	00:02	91.8/8.2	20.3	79.
	C2[c]	100.0	00:04	100/0 (96)	10.9	89.
4	**C1**[a]	99.0	00:02	79.3/20.7	0	10(
	C2[c]	99.0	00:04	99/0 (98)	0	10(
5	**C1**[a]	100.0	00:04	56.8/43.2	0	10(
	C2[c]	100.0	00:04	100/0 (96)	0	10(
6	**C2**[c]	100.0	02:08	100/0 (99)	0	10(
7	**C2**[c]	100.0	07:53	93.2/6.8	0	10(

C1 = Pt-Karstedt; **C2** = [{Rh(μ-Cl)(COD)}$_2$]; **C3** = [$RhCl(PPh_3)_3$]; **C4** = Pt/SD (1% Pt); **C5** = Rh/SDB (1% Rh). Reaction conditions: T=50 °([H_2C=CH-] : [HSi≡] = 1 : 4, [a] - [Pt] : [H_2C=CH-] = $2x10^{-5}$: 1, [b] - [Pt] : [H_2C=CH-] $2x10^{-7}$: 1, [c] - [Rh] : [H_2C=CH-] = $2x10^{-4}$: 1, [d] - [M] : [H_2C=CH-] = 10^{-3} : 1. Time reactions was determined by in situ IR technique and calculated using th intensity of Si-H bond. [d]Conversion yield were determined by GC analysis and calculated on the basis of $ViSiR_3$, using the solvent as a standard. Yield of the isolated product is given in parentheses.

In view of the data reported in publications and patents, in most reactions conducted with unsaturated reagents (organic or organosilicon) at the equimolar ratio with TMDSO or close to this ratio (e.g. 1 : 1.33 or 1.5), selective formation of the monofunctionalized derivatives was problematic, irrespectively

of the catalyst used. The employment of rhodium- ($RhCl_3$, $[RhCl(PPh_3)_3]$, $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$, $[RhCl_3(t\text{-}Bu_2S)_3]$, etc.), or platinum-based catalysts (H_2PtCl_6, Pt-Karstedt, $PtCl_2(PPh_3)_2$, etc.) always led to the formation both, mono- and bishydrosilylation products.[7a,17b,17d,17e,18,23] Thus, in order to quench the reaction at the stage of monofunctionalized product formation, the use of at least twofold, and in some cases, even a tenfold molar excess of TMDSO with respect to the unsaturated reagents was required.[6,11b,12b,17a,17c] However, regardless of the type of catalyst employed, as well as the ratio of the reagents, the reaction of mono hydrosilylation with use of TMDSO, in particular with vinylsilanes or vinylsiloxanes,[17c,17e,19,23] always led to the formation of two isomeric products, which are a result of *α*- or *β*-addition process [24].

Selected derivatives of TMDSO presented in Table 2 were isolated and characterized by spectroscopic methods (see Experimental section and Supporting information), to show the scope of this new versatile and efficient synthetic method enabling the synthesis of coupling agents on the basis of TMDSO – a commercially available and commonly used silicone reagent.

Conclusions

In this report we have presented results of the studies aimed at establishment of the conditions enabling selective monofunctionalization of TMDSO *via* hydrosilylation reaction. Catalytic trials conducted in the reaction systems made of TMDSO and selected vinylsilanes, as well as with use of various homogeneous or heterogeneous platinum and rhodium hydrosilylation promoters (**C1** - **C5**), and additionally monitored by in situ IR technique, have allowed the selection of the most promising catalysts, which showed good selectivity toward the desired products, namely Pt-Karstedt (**C1**) and $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$ (**C2**). Additionally, we found that the complex $[RhCl(PPh_3)_3]$ (**C3**), a commonly applied hydrosilylation catalyst, is much less active than the binuclear rhodium precursor **C1** ($[\{Rh(\mu\text{-}Cl)(COD)\}_2]$). Furthermore, the latter proved to be regioselective towards the formation of *β*-addition products, when used in the reactions of vinyl-silicon compounds with significantly more sterically crowded structure, i.e. bearing in their structure bulky substituents at silicon (-O^{t}Bu or –$SiMe_2N(SiMe_3)_2$. Selected compounds were also isolated and characterized by spectroscopic methods.

Experimental Section

Methods and Materials: Vinyltrimethoxysilane, sodium hydride, Pt-Karstedt catalyst, 1,1,3,3-tetramethyldisiloxane, 1,1,1,3,3,3-hexamethyldisilazane, chlorodimethylvinylsilane, potassium *tert*-butoxide, rhodium(III) chloride hydrate, COD, anhydrous toluene, pentane, ethanol were purchased from Sigma Aldrich. Vinyltriethoxysilane, chlorodiphenylvinylsilane and vinyltrichlorosilane were obtained from ABCR. Vinylmethyldimethoxysilane and diethoxyphenylvinylsilane were purchased from Gelest Inc. All chemicals were used without any further purification. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 300 MHz spectrometer using $CDCl_3$ as solvent. The ^{29}Si NMR spectra were recorded using Bruker Ascend 400 spectrometer. The mass spectra were obtained by GCMS analysis (Bruker MS320 Triple quad, equipped with a VF-5 Factor four capillary column (30 m) and a quadrupole detector). In-situ FT-IR measurements were performed on a Mettler Toledo ReactIR 15 equipped with a DS 6.3mm AgX DiComp Fiber Probe with a diamond sensor, and a Hg-Cd telluride detector. For all the spectra 125 scans were recorded with the resolution of 1 cm^{-1} in 30 s intervals. The $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$, $[RhCl(PPh_3)_3]$ complexes[25] as well as was Pt/SDB (1 w% Pt); **C5** = Rh/SDB (1 w% Rh)[22] were prepared according to the published methods.

Synthesis of tris(*tert*-butoxy)vinylsilane (3): To a suspension of 10 g (89.1 mmol) of potassium *tert*-butoxide in 150 mL of hexane 4.79 g (29.66 mmol) of trichlorovinylsilane was added dropwise at room temperature. After addition of the silicon derivative the resulted mixture was stirred for 24h at room temperature and then refluxed for 2h. After filtration and evaporation of the solvent desired $H_2C{=}CHSi(O^tBu)_3$ was obtained with a yield 95% (7.73 g, 28.17 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 6.02-5.85 (m, 3H, $CH{=}CH_2$), 1.32 [s, 27H, $OC(CH_3)_3$], ^{13}C NMR ($CDCl_3$, δ, ppm): 137.19 ($CH{=}CH_2$), 133.06 ($CH{=}CH_2$), 72.77 [$OC(CH_3)_3$], 31.85 [$OC(CH_3)_3$]. ^{29}Si NMR ($CDCl_3$, δ, ppm): -74.25. MS (EI, m/z): 259.3 (35) [M^+-15], 203.1 (15.9), 147.0 (52.9), 145.0 (29.4), 89.0 (100), 79.0 (20.2), 63.0 (30), 57.1 (64.7).

Synthesis of dimethylvinylsilylbis(trimethylsilyl)amine (5):
To a suspension of 1.636 g (68.2 mmol) NaH in 100 mL of anhydrous toluene 10.2 g (61.9 mmol) of hexamethyldisilazane was added, then the mixture was refluxed for 24h and cooled to room temperature. Next, 8.216 g (68.1 mmol) of chlorodimethylvinylsilane was added dropwise and reaction was continued under reflux for 4 and 6 hours at room temperature. After filtration volatile ingredients including solvent were removed under reduced pressure. Product was purified by the trap-to-trap distillation. Desired product was obtained with yield 78.6 % (12.23 g, 49.8 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 6.30-6.23 (m, 1H $CH{=}CH_2$), 5.91-5.64 (dd, 2H, $CH{=}CH_2$), 0.32-0.06 (m, 24H, CH_3Si). ^{13}C NMR ($CDCl_3$, δ, ppm): 143.69 ($CH{=}CH_2$), 130.34 ($CH{=}CH_2$), 5.68 [$(CH_3)_3Si$], 4.06 [$(CH_3)_2Si$]. ^{29}Si NMR ($CDCl_3$, δ, ppm): 3.07 [$(CH_3)_3Si$], -6.63 [$(CH_3)_2Si$]. MS (EI, m/z): 231.3 (19.2) [M^+-15], 230.2 (100), 203.2 (15.3), 202.1 (67.1), 188.1 (16.0), 142.0 (21.5), 130.0 (35.0), 100.0 (26.6), 73.1(48), 59.0 (32.0).

Synthesis of (Ethoxy)diphenylvinylsilane (7): To a mixture containing 0.564 g (12.24 mmol) of ethanol, 1.65 g (16.30 mmol) of trimethylamine and 10 mL of anhydrous tetrahydrofuran, 2 g (8.17 mmol) of chlorodiphenylvinylsilane was added dropwise at room temperature. Then mixture was stirred at ambient conditions and controlled by GCMS technique. Next, trimethylamine hydrochloride was separated by filtration and washed with cooled THF. Filtrate was placed in the flask and evaporation of solvent and excess of ethanol and trimethylamine gave pure product with yield a 92 % (1.912 g, 7.52 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.68-7-66 (d, 4H), 7.47-7.40 (m, 6H), 6.60-6.48 (m, 1H), 6.35-6.28, 5.99-5.91 (dd, 2H), 3.88 (q, 2H), 1.29 (t, 3H), (^{13}C NMR ($CDCl_3$, δ, ppm): 137.00 ($CH{=}CH_2$), 135.11, 134.52, 133.78 ($CH{=}CH_2$), 130.07, 127.97, 59.70 (OCH_2), 18.55 (CH_3), ^{29}Si NMR ($CDCl_3$, δ, ppm): -14.89; MS (EI, m/z): 254.3 (30.5) [M^+], 227.3 (14.7), 225.3 (22.3), 209.3 (17.8), 208.2 (56.5), 199.2 (17.6), 184.2 (18.8), 183.2 (100), 182.4 (21.9), 181.2 (38.3), 177.2 (21.3), 176.2 (74.8), 150.1 (57.5), 149.1 (28.8), 133.1 (31.6), 132 (16.0), 123.1 (55.1), 105.1 (51.6), 104.0 (53.0), 78.0 (16.8), 77.0 (35.5), 73.1 (21.0).

General procedure for hydrosilylation of vinyl-substituted silicon compounds by 1,1,3,3-tetramethyldisiloxane: A mixture containing 2 g (14.88 mmol) of 1,1,3,3-tetramethyldisiloxane and (7.44 mmol) of vinylsilane was placed in a glass tube (25 mL) and heated at 50 °C, then the catalyst [Rh] : [C=C] = 2 x 10^{-4} : 1, [Pt] : [C=C] = 10^{-5} : 1 was added. Reaction mixture was stirred at 50 °C and monitored by in situ FT-IR spectroscopy to designate the endpoint of process. Then GCMS analysis was performed to calculate conversion of vinylsilane. After cooling to room temperature excess of disiloxane and unreacted vinylsilane were evaporated under vacuum to obtain products. Ratio between mono- and bishydrosilylation products as well as regioisomers were calculated on the basis of GCMS analysis. Signals from α isomers are highlighted in italics.

Spectroscopic data for $HSiMe_2OSiMe_2CH_2CH_2Si(OMe)_3$: (Yield 93%, 6.91 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 4.66 (m, $J_{H\text{-}Si}$ = 198 Hz, 1H, SiH), 3.56 (s, 9H, OCH_3), *1.07*, 0.54 (4H, $SiCH_2$, $SiCHCH_3$) 0.17-0.03 (m, 12H, CH_3Si). ^{13}C NMR ($CDCl_3$, δ, ppm): 50.67(OCH_3), 8,99, 0.96, ($SiCH_2$), *7.60, 5.35* ($SiCHCH_3$),0.66, *0.37, 0.15*, -0.64 (CH_3Si). ^{29}Si NMR ($CDCl_3$, δ, ppm): 10.21, *9.58* [$HSi(CH_3)_2$], -6.65, *-7.16* [$OSi(CH_3)_2CH_2$], -41.55, *-42.37* [$Si(OMe)_3$]. MS (EI, m/z): β_{isomer}: 267.2 (27.3) [M^+-15], 193.0 (25.5), 163.2 (24.3), 133.0 (100), 121.1 (16.8), 91.0 (20.7), 89.1 (24.1), 73.1 (22.0), 59.0 (35,4). MS (EI, m/z): α_{isomer}: 268.2 (21.9), 267.2 (100) [M^+-15], 193.0 (27.8), 164.1 (16.3), 163.0 (25.2), 133.0 (60.1), 117.0 (17), 91.1 (22.9), 90.1 (22.0), 89.1 (23.0), 73.1 (22.5), 59.0 (45.6).

Spectroscopic data for $HSiMe_2OSiMe_2CH_2CH_2Si(OEt)_3$: (Yield 98%, 7.29 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 4.66 (m, $J_{H\text{-}Si}$ = 201 Hz, 1H, SiH), 3.80 (q, 6H, OCH_2CH_3), 1.21 (t, 9H, OCH_2CH_3), *1.05*, 0.54 (4H, $SiCH_2$, $SiCHCH_3$), 0.02-0.17 (m, 12H, CH_3Si). ^{13}C NMR ($CDCl_3$, δ, ppm): 58.50 (OCH_2CH_3), 18.42 (OCH_2CH_3), 9.14, 1.88, ($SiCH_2$), *7.75, 6.06* (SiCHCH3), 0.98, *0.74, 0.08*, -0.61 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, δ, ppm): 10.40, *9.90* ($HSi(CH_3)_2$), -6.73, *-7.45* ($OSi(CH_3)_2CH_2$], *-44.66*, *-45.89* [$Si(OEt)_3$]. MS (EI, m/z): β_{isomer}: 221.2 (22.3), 207.1 (18.7), 205.1 (33.3), 193 (50.5), 163.1 (22.9), 133.0 (100) 119.0 (21.9), 79.0 (15.4), 73.1 (25.2). MS (EI, m/z): α_{isomer}: 310.3 (18.5), 309.2 (72.8) [M^+-15], 251.2 (21.9), 237.2 (17.6), 236.2 (18.3), 235.2 (87.2), 223.2 (20.4), 221.2 (41.2), 207.1 (30.0), 206.2 (21.6), 205.1 (100), 195.1 (18.1), 194.2 (20.9), 193.1 (98.8), 192.3 (19.9), 179.0 (61.1), 177.0 (32.1), 163.0 (37.4), 147.1 (16.0), 135.0 (20.9), 133.0 (93.5), 119.1 (36.1), 117.0 (23.5), 103.0 (21.0), 91.1 (20.3), 79.1 (23.6), 73.1 (51.2), 63.0 (15.9), 59.0 (26.5).

Spectroscopic data for $HSiMe_2OSiMe_2CH_2CH_2SiMe(OMe)_2$: (Yield 96%, 7.14 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 4.66 (m, $J_{H\text{-}Si}$ = 204 Hz, 1H, SiH), 3.49 (s, 6H, OCH_3), *1.03,* 0.5 (4H, $SiCH_2$, $SiCHCH_3$), 0.02-0.16 (m, 15H, CH_3Si), ^{13}C NMR ($CDCl_3$, δ, ppm): 50.31 (OCH_3), 8.99, 4.34 ($SiCH_2$), 0.99, 0.63, -6.51 (CH_3Si). ^{29}Si NMR ($CDCl_3$, δ, ppm): 10.35 [$HSi(CH_3)_2$], 0.70 [$OSi(CH_3)_2CH_2$], -6.71 [$CH_3Si(OCH_3)_2$]. MS (EI, m/z): β_{isomer}: 251.2 (23.0) [M^+-15], 177.1 (23.1), 176.1 (16.9), 163.1(26.6), 161.1 (15.4), 133.0 (100), 105.0 (46.1), 89.0 (25.1), 75.1 (29.7), 73.2 (28.6), 59.0 (29.9). MS (EI, m/z): α_{isomer}: 252.2 (23.9), 251.2 (100) [M^+-15], 177.1 (30.9), 176.0 (18.6), 163.1 (26.1), 133.1(53.7) 119.1 (16.1), 117.0 (16.3), 105.1 (26.8), 103.0 (19.7), 102.0 (22.7), 89.0 (33.4), 75.1 (30.7), 74.1 (28.6), 73.1 (34.6), 59.0 (42.3),

Spectroscopic data for $HSiMe_2OSiMe_2CH_2CH_2Si(O^tBut)$: (Yield 98%, 7.29 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 4.71 (m, $J_{H\text{-}Si}$ = 201 Hz, 1H, SiH), 1.30 [s, 27H, $OC(CH_3)_3$], 0.60-0.36 (m, 4H, $SiCH_2$), 0.19-0.07 (m, 12H, CH_3Si). ^{13}C NMR ($CDCl_3$, δ, ppm): 72,13 [$OC(CH_3)_3$], 31.84 [$OC(CH_3)_3$], 10.41, 8.84 ($SiCH_2$), 1.01, 0.42 (CH_3Si). ^{29}Si NMR ($CDCl_3$, δ, ppm): 10.94 [$HSi(CH_3)_2$], -7.06 [$OSi(CH_3)_2CH_2$], -59.86 [$Si(O^tBut)_3$]. MS (EI, m/z): β_{isomer}: 247.3 (9.4), 239.2 (5.1), 221.1 (9.4), 205.1 (12.2), 191.1 (9.5), 136.2 (7.7), 135.0 (84.7), 133.0 (16.3) 121.0 (6.2), 119.1 (5.1), 79.0 (31.5), 73.1 (5.8), 57.1 (100).

Spectroscopic data for $HSiMe_2OSiMe_2CH_2CH_2Si(Me)_2N(SiMe_3)_2$: (Yield 96%, 7.14 mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 4.7 (m, $J_{H\text{-}Si}$ = 201 Hz, 1H, SiH), 0.56-0.38 (m, 4H, $SiCH_2$), 0.194-0.165 (m, 30H, CH_3Si), 0.07 [s, 6H, $(CH_3)_2SiN$]. ^{13}C NMR ($CDCl_3$, δ, ppm): 12.03, 10.53 ($SiCH_2$), 5.74 [$(CH_3)_3Si$], 3.19, 1.09, 0.45 (CH_3Si). ^{29}Si NMR ($CDCl_3$, δ, ppm): 10.63 [$HSi(CH_3)_2$], 5.07 [$OSi(CH_3)_2CH_2$], 2.27 [$(CH_3)_3Si$], -6.83 [$(CH_3)_2SiN$]. MS (EI, m/z): β_{isomer}: 220.3 (11.5), 219.3 (21.7), 218.2 (100), 216.2 (22.3), 202.3 (11.6), 134.2 (7.5), 133.1 (48.2), 132.2 (8.2), 131.1 (7.0), 130.0 (31.0), 100.0 (7.6), 73.1 (28.6), 59.0 (8.4).

Spectroscopic data for $HSiMe_2OSiMe_2CH_2CH_2SiPh_2OEt$: (Yield 99%, 7.36mmol). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.64-7.61 (d, 4H), 7.43-7.40 (m, 6H), 4.72 (m, $J_{H\text{-}Si}$ = 201 Hz, 1H, SiH), 3.80 (q, 2H, OCH_2), 1.24 (t, 3H, OCH_2CH_3), 1.11, 0.57 (m, 4H, $SiCH_2CH_2$), 0.18-0.09 (m, 12H, $Si(CH_3)_2$. 13C NMR ($CDCl_3$, δ, ppm): 135.26, 134.91, 129.86, 127.94 (C_{phenyl}), 59.41 (OCH_2), 19.06 (OCH_2CH_3), 9.34, 5.21 ($SiCH_2CH_2$), 1.05, 0.49 (CH_3Si). ^{29}Si NMR ($CDCl_3$, δ, ppm): 10.51 [$HSi(CH_3)_2$], -3.57 [$OSi(CH_3)_2CH_2$], -6.56 [$(Ph)_2Si$], MS (EI, m/z): β_{isomer}: 359.2 [M-Et] (5.2), 311.2 (5.2), 281.2 (13.1), 229.3 (5.3), 228.3 (19.7), 227.2 (100), 199.2 (9.8), 197.2 (5.4), 184.2 (11.2), 183.1 (65.5), 160.1 (6.0), 145.1 (8.9), 135.1 (13.1), 133.1 (31.5), 132.4 (7.5), 123.0 (40.2), 121.0 (9.5), 105.0 (12.8), 103.0 (6.8), 77.1 (15.8), 73.1 (20.5), 59.0 (8.5).

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