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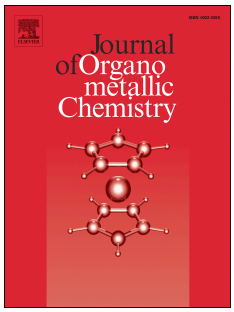

An efficient catalytic and solvent-free method for the synthesis of mono-organofunctionalized 1,1,3,3-tetramethyldisiloxane derivatives

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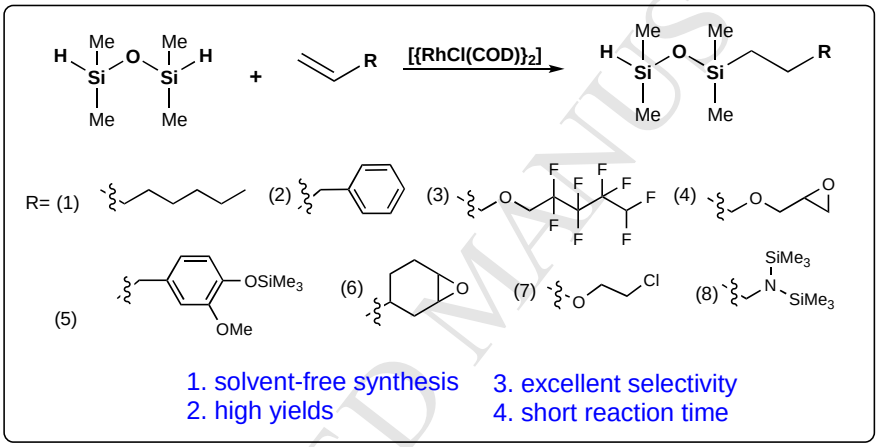
Graphical abstract



An efficient catalytic and solvent-free method for the synthesis of mono-organofunctionalized 1,1,3,3-tetramethyldisiloxane derivatives

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Abstract

Selective mono-functionalization of 1,1,3,3-tetramethyldisiloxane (TMDSO) with olefins *via* hydrosilylation reaction is reported. On the basis of a study of platinum- and rhodium complexes in the reactions between TMDSO and selected olefins containing C=C bond, it was possible to choose the most efficient catalyst whose application in the solvent-free system led to selective mono-functionalization of the disiloxane reagent and simultaneous formation of only *β*-regioisomeric products, bearing in their structure functional groups of unique reactivity or physicochemical properties.

Keywords: Rhodium complexes, Homogeneous catalysis, Selective hydrosilylation, Siloxanes

1. Introduction

In the silicon industry, the reaction of hydrosilylation is considered the most important one and is commonly used in a large-scale synthesis of a wide range of organosilanes or organosiloxanes as well as for cross-linking of silicone fluids [1], including silyl-functionalization of unsaturated organic [2] or organosilicon [3] of polymers for different applications, depending on the type and reactivity of the introduced functional groups. The importance of functionalized silicon hydrides is illustrated by the number of patents, which have appeared for the last 20 years. The synthesis and utilization of organic and organosilicon polymers equipped with reactive functional groups of various types has been a focus of growing interest [3-7]. For instance, partly modified with organic groups 1,1,3,3-tetramethyldisiloxane (TMDSO) derivatives are widely used in the synthesis of dendrimers [8,9], liquid crystals [10], hyperbranched polymers [11], solid polymeric electrolytes [12], coupling agents [13,14] or monomers for UV induced polymerization [15].

The conventional synthetic route to obtain unsymmetrical functionalized siloxanes involves condensation reactions of silanols with chloro-, acyloxy, amino- or alkoxysilanes, and co-hydrolysis of

two chloro- or alkoxysilanes [16]. In recent years, we have observed a growing number of catalytic methods for the synthesis of new unsymmetrical organosilicon compounds, such as reduction of amides by hydrodisilanes in the presence of [(Me_3N) $Mo(CO)_5$] catalyst [17], scandium(III)-catalyzed hydrolysis of alkoxysilanes and O-silylation of silanols with 2-methylallylsilanes [18] as well as dehydrocoupling of silanols with hydrosilanes in the presence of rhodium(I) complexes [19]. In view of literature data, the hydrosilylation reaction is the most convenient and widely used protocol for obtaining new organosilicon compounds. The hydrosilylation reaction, in most cases, is catalyzed by transition metal complexes, in particular Rh (Wilkinson's catalyst) and Pt (Karstedt's catalyst, H_2PtCl_6), allowing functionalization of TMDSO core with organic groups, such as organic epoxides [11a], aryloxyalkyl or arylalkyl [10a,10c,15b,22], PEG of different lengths [8a,10d], 3-(alkoxy) propyl [8a], 3-(methacryloxy) propyl [11b,20], 3-(benzophenoxy) propyl [21] and 3-(amino) propyl [9a,23].

The paper provides a discussion on the studies concerning the selective, high-yield mono-functionalization of TMDSO with olefins via the rhodium(I)-catalyzed hydrosilylation reaction leading to the formation of β-addition products. All products were characterized by NMR (^1H, ^{13}C, ^{29}Si) and GCMS analysis. This type of bifunctional compounds are based on flexible disiloxane core and bear two reactive moieties in its structure, i.e. HSi≡ moiety, which can take part in hydrosilylation process, and an organic functional group that determines their properties. They seem to be very interesting from the practical point of view, as they can also be used as modifiers of vinyl containing molecular or macromolecular organosilicon materials, as well as unsaturated polymeric organic systems. Particularly interesting are mono-functionalized siloxane derivatives equipped with moieties of unique properties e.g. fluoroalkyl, chloroalkyl, alkyl, arylalkyl or reactive alkoxysilyl- and epoxy- functionalities.

2. Experimental section

2.1 Methods and techniques

1,1,3,3-tetramethyldisiloxane, Karstedt catalyst, hexamethyldisilazane, rhodium(III) chloride hydrate, 1,4-cyclooctadiene, 1-octene, 2-chloroethyl vinyl ether, allyl chloride, allylbenzene, allyl glycidyl ether, 4-Vinyl-1-cyclohexene 1,2-epoxide, mixture of isomers, N-allyl-N, N-bis(trimethylsilyl) amine were purchased from Sigma-Aldrich, eugenol was obtained from Acros Organics, solvents were purchased from POCH. All chemicals were used without any further purification. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 300 MHz spectrometer using $CDCl_3$ as a 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). The [{Rh(μ-Cl)(COD)}$_2$], [RhCl(PPh$_3$)$_3$] complexes [25] were prepared according to the published methods.

2.2 Synthesis of olefins

2.2.1 2-methoxy-4-allylphenyltrimethylsilyl ether: To a 10 g (60.90 mmole) of eugenol (31.97 mmole) of hexamethyldisilazane was added and the mixture was refluxed for 4 hours. Then the excess of silazane was evaporated under vacuum to obtain desired product with yield 98% (14.10 g, 59.68 mmole). ^{1}H NMR (CDCl$_3$, δ, ppm): 6.80-6.64 (m, 3H), 6.05-5.92 (m, 1H CH=CH$_2$), 5.12-5.06 (m, 2H CH=CH$_2$), 3.81 (s, 3H OCH$_3$), 3.34 (d, 2H CH$_2$), 0.25 (s, 9H Si(CH$_3$)$_3$). ^{13}C NMR (CDCl$_3$, δ, ppm): 150.83, 142.85, 137.81, 133.74, 120.79, 120.71, 115.68, 112.58, 55.57, 40.03, 0.42. MS (EI, m/z): 236.3 (39.3) [M$^+$], 221.3 (23.3), 207.2 (22.6), 206.2 (100), 205.2 (40.9), 179.1 (11.6), 92.2 (10.2), 91.2 (12.2), 75.3 (10.4), 73.2 (31.6).

2.2.2. 5-Allyl-1,1,2,2,3,3,4,4- octafluoropentyl ether: To a dispersion prepared of 11.22g (0.2 mole) of KOH and 100mL of acetonitrile, a portion of 46.4 g (0.2 mole) of 1,1,2,2,3,3,4,4-octafluoropentan-5-ol was added and the mixture was stirred at r.t. for 1.5h, then 0.22 mole of allyl chloride was added. Then mixture was refluxed for 5 hours and kept at r.t. for 24 hours. The precipitate was separated by filtration and was washed with cold acetonitrile. The solvent was removed by rotary evaporation and obtained product was purified by trap to trap distillation to give colorless liquid yield 89%.^{1}H NMR (CDCl$_3$, δ, ppm): 6.96 (m, 1H, CHF$_2$), 5.79 (m, 1H, CH=CH$_2$), 5.19 (t, 2H, CH$_2$=CH-), 4.04 (d, 2H, CH$_2$O), 3.81 (t, 2H, OCH$_2$CF$_2$),^{13}C NMR (CDCl$_3$, δ, ppm): 133.09 (CH=CH$_2$), 118.98 (CH$_2$=CH), 115.66 (CF$_2$), 111.13 (CF$_2$H), 107.77 (CF$_2$), 104.40 (CF$_2$), 73.55 (CH$_2$O), 66.42 (OCH$_2$). MS (EI, m/z): 273.3 (10.1), 272.2 (91.0) [M$^+$], 95.0 (14.6), 84.0 (9.3), 71.1 (100), 69.1 (26.1), 57.1 (23.3), 56.1 (9.4), 51.0 (31.7).

2.2.2. General procedure for hydrosilylation of olefins by 1,1,3,3-tetramethyldisiloxane (TMDSO): A mixture containing 1 g (7.44 mmole) of 1,1,3,3-tetramethyldisiloxane and (3.72 mmole) of alkene was placed in a glass tube (25 mL) and stirred. Then the catalyst [Rh]: [C=C] = 2 x 10^{-4}: 1, [Pt]: [C=C] = 10^{-5}: 1 was added and the mixture was heated at 50^{o}C until the complete achievement of alkene conversion. The reactions were monitored by GC and GCMS analyses. **C1** and **C3** required two hours, while **C2 -** three hours. Then GCMS analysis was performed to calculate the degree of alkene conversion. After cooling it to room temperature, the excess of TMDSO was evaporated under vacuum to obtain products. Ratios between mono- and bishydrosilylation products as well as regioisomers were calculated based on GCMS analysis.

2.3. Spectroscopic data of obtained compounds via selective functionalization of TMDSO

2.3.1. $HSiMe_2OSiMe_2(CH_2)_7CH_3$: ^{1}H NMR ($CDCl_3$, δ, ppm): 4.69 (m,1H SiH), 1.27 (s, 12H, CH_2), 0.89 (t, 3H, CH_3), 0.53 (t, 2H $SiCH_2$), 0.16, 0.06 (12H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 33.58, 32.12, 29.51, 29.44, 23.35, 22.86, 18.30, 14.27 ($SiCH_2$), 1.06, 0.20 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, δ, ppm): 9.93 [$HSi(CH_3)_2$], -6.99 [$Si(CH_3)_2CH_2$], MS (EI, m/z): 231.3 (4.3) [M^+-15], 135.1 (7.2), 134.2 (14.3), 133.1 (100), 119.1 (37.1), 117.1 (6.7), 103.0 (5.8), 73.2 (17.3), 59.1 (6.0).

2.3.2. $HSiMe_2OSiMe_2CH_2CH_2CH_2Ph$: ^{1}H NMR ($CDCl_3$, δ, ppm): 7.23-7.07 (m, 5H), 4.62 (m, 1H SiH), 2.56 (t, 2H CH_2), 1.59 (m, 2H, CH_2), 0.52 (t, 2H $SiCH_2$), 0.12-0.00 (12H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 142.80, 128.64, 128.38, 125.79, 39.80, 25.49, 18.13 ($SiCH_2$), 1.05, 0.19 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, δ, ppm): 9.77 [$HSi(CH_3)_2$], -6.69 [$Si(CH_3)_2CH_2$], MS (EI, m/z): 252.2 (3.0) [M^+], 161.1 (5.2), 135.2 (6.3), 134.2 (13.1), 133.1 (100), 119.0 (14.1), 117.0 (6.6), 103.0 (9.6), 91.1 (12.3), 73.2 (21.0), 59.1 (9.6).

2.3.3. $HSiMe_2OSiMe_2CH_2CH_2CH_2OCH_2(CF_2)_3CHF_2$: ^{1}H NMR ($CDCl_3$, δ, ppm): 6.06 (m, 1H CF_2H), 4.68 (m, 1H SiH), 3.92 (t, 2H OCH_2), 3.56 (t, 2H CH_2O), 1.64 (m, 2H, CH_2), 0.54 (t, 2H $SiCH_2$), 0.17, 0.08 (12H, $SiCH_3$) ^{13}C NMR ($CDCl_3$, δ, ppm): 115.72, 111.16, 107.83, 104.47, 75.90, 67.66, 23.40, 13.90 ($SiCH_2$), 0.93, 0.01 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, δ, ppm): 9.74 [$HSi(CH_3)_2$], -6.37 [$Si(CH_3)_2CH_2$], MS (EI, m/z): 155.1 (30.0), 152.2 (5.9), 151.1 (41.6), 137.0 (33.6), 135.1 (9.7), 134.2 (13.2) 133.1 (100), 121.0 (5.4), 117.1 (6.3), 103.0 (6.6), 77.2 (10.5), 73.2 (24.5), 71.2 (6.7), 51.9 (9.8), 51.1 (6.5).

2.3.4. $HSiMe_2OSiMe_2CH_2CH_2CH_2OCH_2CH(O)CH_2$: ^{1}H NMR ($CDCl_3$, δ, ppm): 4.64 (m, 1H SiH), 3.68, 3.10 (2H O-CH_2), 3.44-3.32 (m, 3H CH-CH_2), 2.74, 2.56 (2H, CH_2-O), 1.58 (m, 2H, CH_2), 0.50 (t, 2H $SiCH_2$), 0.12, 0.03 (12H $SiCH_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 74.30, 71.48, 50.90, 44.32, 23.46, 14.08 ($SiCH_2$), 0.92, 0.00 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, δ, ppm): 9.82 [$HSi(CH_3)_2$], -6.67 [$Si(CH_3)_2CH_2$], MS (EI, m/z): 175.1 (6.7), 163.1 (5.9), 149.1 (7.7), 135.1 (12.7), 134.1 (14.3), 133.0 (100), 119.0 (6.8), 73.1 (9.4), 59.1 (5.5).

2.3.5. $HSiMe_2OSiMe_2CH_2CH_2CH_2Ph(OMe)(OSiMe_3)$:

^{1}H NMR ($CDCl_3$, δ, ppm): 6.83-6.63 (m, 3H), 4.71 (m, 1H SiH), 3.82 (s, 3H OCH_3), 2.58 (t, 2H, CH_2), 1.65 (m, 2H CH_2), 0.60 (t, 2H $SiCH_2$), 0.26 (s, 9H $Si(CH_3)$), 0.18, 0.09 (12H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 150.65, 142.52, 136.45, 120.62, 112.57, 55.58, 39.43, 25.50, 18.05 ($SiCH_2$), 1.03 ($OSiMe_3$), 0.44, 0.19 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, δ, ppm): 20.11 ($OSiMe_3$), 9.81 [$HSi(CH_3)_2$], -6.74 [$Si(CH_3)_2CH_2$], MS

(EI, m/z):371.4 (14.6), 370 (43.5), 339.3 (6.4), 210.4 (6.7), 209.3 (37.0), 179.2 (26.5), 163.2 (8.4), 147.2 (6.0), 135.3 (6.6), 134.3 (9.3), 133.1 (100), 117.2 (6.6), 73.2 (41.0), 59.0 (7.5).

2.3.6. $HSiMe_2OSiMe_2CH_2CH_2CH_2C_6H_9O$: ^{1}H NMR ($CDCl_3$, δ, ppm): 4.67 (m, 1H SiH), 3.47-3.12 (2H, CH) 2.20-0.88 (m, 9H), 0.50 (m, 2H $SiCH_2$) 0.16, 0.05 (12H, $SiCH_3$) ^{13}C NMR ($CDCl_3$, δ, ppm): 53.44-52.12 (CHO), 35.52-23.74 (CH, $CH_{2\text{-cyclohexyl}}$, CH_2) 15.14 ($SiCH_2$), 1.05, 0.05 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, δ, ppm): 10.07 [$HSi(CH_3)_2$], -6.74 [$Si(CH_3)_2CH_2$], MS (EI, m/z): 149.1 (23.1), 135.1 (27.6) 134.2 (13.3), 133.1 (100), 132.2 (7.0), 119.0 (18.4), 117.3 (7.9), 93.2 (9.4), 81.2 (11.5), 80.1 (16.2), 79.2 (11.7), 75.1 (9.3), 73.2 (27.2), 67.2 (23.6), 59.2 (13.0), 55.0 (8.6), 54.1 (10.6).

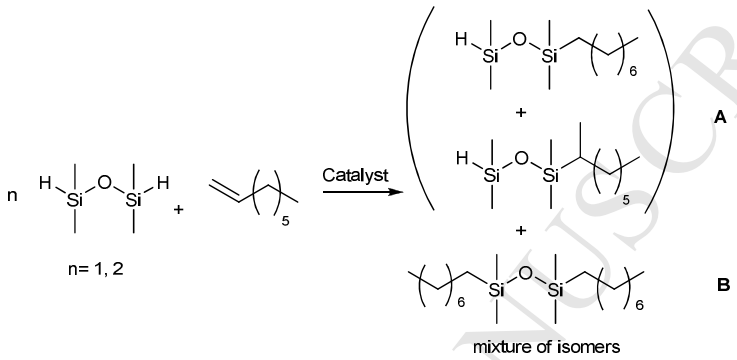
2.3.7. $HSiMe_2OSiMe_2CH_2CH_2OCH_2CH_2Cl$: ^{1}H NMR ($CDCl_3$, δ, ppm): 4.67 (m, 1H SiH), 3.62 (m, 6H, CH_2OCH_2, CH_2Cl), 1.01 (t, 2H $SiCH_2$), 0.17, 0.10 (12H, $SiCH_3$), ^{13}C NMR ($CDCl_3$, δ, ppm): 70.41, 67.95 (CH_2OCH_2), 42.99 (CH_2Cl), 19.90 ($SiCH_2$), 0.97, 0.65 ($SiCH_3$), ^{29}Si NMR ($CDCl_3$, δ, ppm): 7.99 [$HSi(CH_3)_2$], -6.22 [$Si(CH_3)_2CH_2$], MS (EI, m/z): 171.1 (8.3), 170.1 (6.0), 169.0 (38.0), 167.0 (16.7), 163.1 (5.1), 155.0 (24.3), 154.1 (10.4), 153.0 (70.7), 135.2 (5.5), 134.2 (12.8), 133.0 (100), 116.9 (5.0), 102.9 (5.3), 73.2 (32.6), 66.2 (7.2), 59.0 (28.2).

2.3.8. $HSiMe_2OSiMe_2CH_2CH_2CH_2N(SiMe_3)_2$: ^{1}H NMR ($CDCl_3$, δ, ppm): 4.69 (m, 1H SiH), 2.71 (t, 2H NCH_2), 1.34 (m, 2H CH_2), 0.40 (t, 2H $SiCH_2$), 0.17, 0.07 (6H $SiCH_3$), 0.08 (18H, $NSiMe_3$), ^{13}C NMR ($CDCl_3$, δ, ppm): 49.25 (NCH_2), 29.11(CH_2), 15.64 ($SiCH_2$), 2.24 ($NSiCH_3$),1.06, 0.12 ($SiCH_3$), ^{29}Si NMR ($CDCl_3$, δ, ppm): 9.58 [$HSi(CH_3)_2$], 5.13 ($NSiMe_3$), -6.80 [$Si(CH_3)_2CH_2$], MS (EI, m/z): 176.2 (9.1), 175.2 (17.3), 174.3 (100), 172.4 (11.4), 133.0 (14.4), 86.0 (9.3), 73.1 (35.8), 59.1 (9.3).

3. Results and discussion

The work presented in this paper is a continuation of previously reported studies on selective hydrosilylation of organosilicon compounds [14], containing in their structure an unsaturated carbon-carbon double bond, by 1,1,3,3-tetramethyldisiloxane (TMDSO). The mono-functionalization process leads to the corresponding bifunctional organosilicon modifiers having in their structure simultaneously the HSi≡ bond and other silicon-based groups, which have a significant impact on their properties and reactivity. In the previous publication, we have presented the modification of TMDSO by vinyl-substituted silicon compounds catalyzed by rhodium(I) complex [14]. This paper is focused on the investigation concerning the reactivity of alkenes in the reaction with TMDSO.

Therefore, in order to find the best conditions enabling the efficient synthesis of mono-functionalized TMDSO derivatives, the same homogeneous catalytic systems as in the previous work were tested in the model reaction based on 1,1,3,3-tetramethyldisiloxane and 1-octene in the presence of Pt-based Karstedt's complex (**C1**) as well as two rhodium catalysts [$RhCl(PPh_3)_3$] [1] (**C2**) and [{Rh(μ-Cl) (COD)}$_2$] [1] (**C3**) known as effective hydrosilylation promoters. The test reactions were carried out at the equimolar ratio and in the presence of TMDSO excess. (Scheme 1).



Scheme 1. Products distribution in model reaction.

The results, summarized in Table 1, show that in the studied reaction the catalysts (**C1-C3**) proved to be very effective under mild conditions (50^{o}C). However, in all tests carried out at the stoichiometric ratio the mono-functionalized product **A** was accompanied by undesirable derivative **B**.

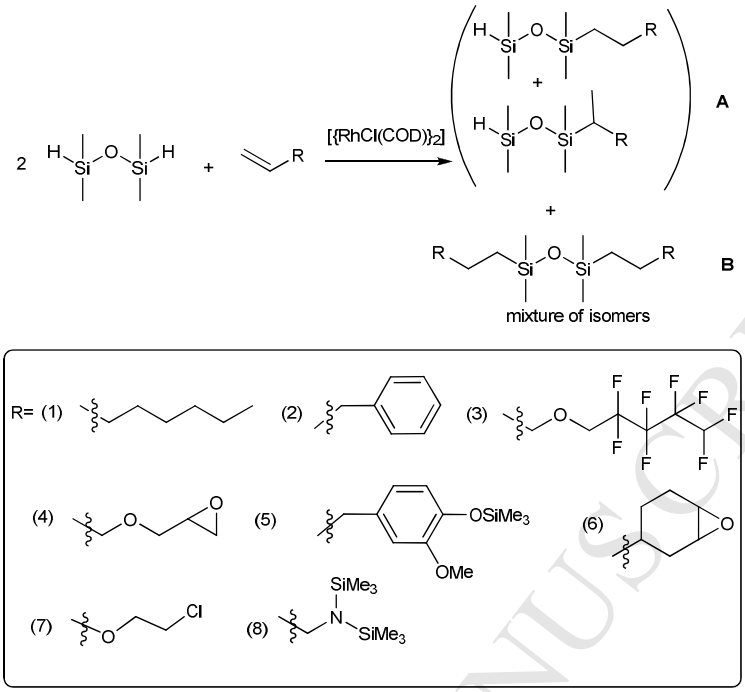
Table 1. Hydrosilylation of 1-octene by 1,1,3,3-tetramethyldisiloxane.

Catalyst	1-octene conversion(%)	Products distribution (%)		Product **A** regioselectivity (%)	
		A	**B**	**α**	**β**
C1[a]	100	66.2	33.8	0.5	99.5
C1[b]	100	67.2	32.8	1.0	99.0
C2[c]	100	83.4	16.6	1.5	98.5
C2[d]	100	95.5	4.5	1.6	98.4
C3[c]	100	88.7	11.3	1.6	98.4
C3[e]	100	88.6	11.4	1.4	98.6

C3[f]	100	93.6	6.4	0.5	99.5
C3[g]	100	92.2	7.8	0.4	99.6
C3[d]	100	100	0	0.9	99.1

C1 = Pt-Karstedt's; **C2** = $[RhCl(PPh_3)_3]$; **C3** = $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$; Reaction conditions: [a] - $[H_2C{=}CH\text{-}]$: [HSi≡] = 1 : 2, [Pt] : $[H_2C{=}CH\text{-}]$ = $2x10^{-5}$: 1, [b] - $[H_2C{=}CH\text{-}]$: [HSi≡] = 1 : 4, [Pt] : $[H_2C{=}CH\text{-}]$ = $2x10^{-5}$: 1, [c] - $[H_2C{=}CH\text{-}]$: [HSi≡] = 1 : 2, [Rh] : $[H_2C{=}CH\text{-}]$ = $2x10^{-4}$: 1, [d] - $[H_2C{=}CH\text{-}]$: [HSi≡] = 1 : 4, [Rh] : $[H_2C{=}CH\text{-}]$ = $2x10^{-4}$: 1, [e] - $[H_2C{=}CH\text{-}]$: [HSi≡] = 1 : 2, [Rh] : $[H_2C{=}CH\text{-}]$ = $2x10^{-4}$: 1, concentration of reagents in hexane – 50%, [f] - $[H_2C{=}CH\text{-}]$: [HSi≡] = 1 : 2, [Rh] : $[H_2C{=}CH\text{-}]$ = $2x10^{-4}$: 1, concentration of reagents in hexane – 25%, [g] - $[H_2C{=}CH\text{-}]$: [HSi≡] = 1 : 2, [Rh] : $[H_2C{=}CH\text{-}]$ = $2x10^{-4}$: 1, concentration of reagents in hexane – 10%

Moreover, the selectivity of platinum Karstedt's catalyst (**C1**) was very poor, when compared to that of rhodium based pre-catalysts (**C2-C3**). Furthermore, the excess of TMDSO in the reaction catalyzed by **C1** had no significant effect on the distribution of products, in contrast to the results obtained from trials performed in the presence of complexes **C2** and **C3.** The model reactions carried out at the equimolar ratio showed that the most advantageous proportion between the mono-functionalized product **A** and the bisubstituted product **B** was obtained in the presence of **C3** as a promoter. To our surprise, dilution of the reaction system by hexane did not bring considerable changes in the products distribution, and in these reactions, the formation of product **B** was always observed. Therefore, it seemed obvious that the increase in the molar ratio of TMDSO to 1-octene from 1 : 1 to 2 : 1, should have a significant impact on the products distribution in such reaction systems, wherein the molar ratio of HSi≡ bond to alkene reagent formally is 4 : 1. Using the commonly known Wilkinson's catalyst (**C2**) in the presence of TMDSO excess, a total conversion of 1-octene was obtained after two hours as well as a high selectivity in formation of product **A** (95.5%) was observed. However, in the same conditions, rhodium-based catalyst **C3** leads only to the selective formation of product **A** with the vast predominance of *β*-regioisomer. Therefore, in successive stages, i.e. in the reactions between TMDSO and alkenes containing different groups such as alkyl, alkyaryl-, epoxy, fluoroalkyl and silyl ether, only catalyst **C3** was examined (Scheme 2).



Scheme 2. Products distribution in the rhodium(I)-catalyzed reaction of TMDSO with selected olefins in the molar ratio 2: 1.

The results compiled in Table 2 show that the selected rhodium binuclear precursor **C3** proved to be an efficient TM-based homogenous catalyst, which smoothly promoted the addition of HSi≡ unit to the carbon-carbon double bond in a wide range of alkenes of various structures as well as bearing different functional moieties. Furthermore, in the reactions carried out in the systems in which an excess of 1,1,3,3-tetramethyldisiloxane relative to the alkenes was applied, the formation of monofunctionalized product **A** was always observed. Moreover, the catalytic activity and selectivity was confirmed by high isolated yield of the obtained partly functionalized TMDSO derivatives, wherein the predominance of *β*-regioisomers was confirmed by GCMS and NMR techniques. Nonetheless, the highest amount of *α*-regioisomers was observed for allyl ethers (**3,4**). However, no alpha-isomeric products were found in the post-reaction mixtures for compounds containing in their structure six-membered rings such as cyclohexyl (**6**) or phenyl (**2,5**) and for (**7**) and (**8**).

Table 2. Hydrosilylation of alkenes by 1,1,3,3-tetramethyldisiloxane

Alkene	Alkene conversion (%)	Products distribution (%)		Product **A** regioselectivity (%)		Yield of isolated product (%)
		A	**B**	**α**	**β**	
1	100	100	0	0.9	99.1	99
2	100	100	0	0	100	99
3	100	100	0	1.6	98.4	92
4	100	100	0	4.8	95.2	98
5	100	100	0	0	100	99
6	100	100	0	0	100	98
7	100	100	0	0	100	93
8[a]	100	100	0	0	100	96

Reaction conditions: T=50 ^{o}C, t= 2 h, [H_2C=CH-] : [HSi≡] = 1 : 4, [Rh] : [H_2C=CH-] = $2x10^{-4}$: 1,

[a] - T=50 ^{o}C, t= 2 h, [H_2C=CH-] : [HSi≡] = 1 : 4, [Rh] : [H_2C=CH-] = 10^{-3} : 1

All the functionalized 1,1,3,3-tetramethyldisiloxane derivatives presented in Table 2 were isolated and characterized by spectroscopic methods such as NMR (^{1}H, ^{13}C and ^{29}Si) and GCMS analysis (see experimental part and Supplementary material) to show the scope of this new versatile and efficient solvent-free method for the synthesis of new TMDSO-based compounds.

As mentioned in the introduction, organofunctionalized unsymmetrical siloxanes importance follows from their wide application. However, in view of the data reported in publications and patent applications, a selective functionalization of TMDSO was problematic. TM catalysts based on rhodium ($RhCl_3$, $[RhCl(PPh_3)_3]$, $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$, $[RhCl_3(tBu_2S)_3]$, etc.) and platinum (H_2PtCl_6, Pt-Karstedt, $PtCl_2(PPh_3)_2$, etc.) always led to formation of a mixture of mono- and disubstituted products, when the ratio of the reagents was close to equimolar [7a,24]. Therefore, the partly modified TMDSO derivatives were prepared mainly using an excess of organosilicon compound, even a tenfold molar excess of disiloxane with respect to the unsaturated reagents [6,8a,9a,10d,f,g;12], or were obtained with poor yield [8a,10d,e,20]. In most cases such unsymmetrical disiloxanes were characterized only by ^{1}H NMR spectroscopy [8a,9a,10a-d, 10f, g,11a,12,20,23].

4. Conclusions

The aim of the study reported was to establish the conditions enabling selective modification of 1,1,3,3-tetramethyldisiloxane by alkenes containing different organic groups *via* hydrosilylation reaction. Catalytic tests showed that the examined catalysts based on platinum (**C1**) and rhodium (**C2, C3**) proved to be effective promoters for hydrosilylation reaction under mild conditions in a solvent-free system. However, commonly known Karstedt's complex (**C1**) was found to be non-selective catalyst even in the presence of an excess of TMDSO. Significantly higher selectivity were obtained using rhodium promoters (**C2, C3**). Though Wilkinson rhodium pre-catalyst (**C2**) provided the formation of monosubstituted TMDSO with high selectivity (95% in the reaction with 1-octene). Unfortunately, the undesirable product of bishydrosilylation was also generated. On the other hand, the rhodium binuclear complex (**C3**) always led to the formation of partially functionalized disiloxane with wide range of alkenes. All mono-organomodified TMDSO derivatives were also isolated with high yield and characterized by spectroscopic methods.

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Research highlights

- studies of TM-promoted hydrosilylation reaction
- efficient and solvent-free selective partial functionalization of TMDSO
- selective formation of *β*-regioisomeric products
- high yield of TMDSO derivatives bearing in their structure functional groups of unique properties or reactivity